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Vol. XXIII. Part 1. JANUARY, 1927.

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## Contents.

Vapour Pressure and Heat of Dilution of Aqueous Solutions. Parts II and III. By W. R. Harrison and E. P. Perman . . .	1
Condition of Silver Chromate in Gelatine from Electric Conductivity and Diffusion Experiments. By A. C. Chatterji and N. R. Dhar . . .	23
The Actinic Absorption of Chlorine Gas, with Respect to the Hydrogen Chlorine Reaction. By W. Taylor . . .	31
The Residual Effect in the Actinic Absorption of Chlorine. By W. Taylor and A. Elliott . . .	38
The Electrostatic Capacity of Aluminium and Tantalum Anode Films. By N. A. de Bruyne and R. W. W. Sanderson . . .	42
The Behaviour of the Quinhydrone Electrode in Solutions of Neutral Copper Sulphate. By J. B. O'Sullivan . . .	52
Reviews of Books . . . . .	56

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Vol. XXIII. Part 2. MARCH, 1927.

Price 5s.

## Contents.

	PAGE
On the Velocity of Chemical Reaction in the Silent Electric Discharge. By G. A. Elliott, S. S. Joshi, and R. W. Lunt . . . . .	57
The Activation of Hydrogen in the Electric Discharge. By G. A. Elliott .	60
The Soret Effect. Part I. By C. C. Tanner . . . . .	75
An Improved Method of Measuring Vapour Pressure by Air Bubbling. By H. I. Downes, and E. P. Perman . . . . .	95
Discussion on Papers in Part I. . . . .	106
Reviews . . . . .	108

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Vol. XXIII.

APRIL, 1927.

Price 7s. 6d.

## Contents.

### Second Experimental Report to the Atmospheric Corrosion Research Committee (British Non-Ferrous Metals Research Association).

BY DR. W. H. J. VERNON.

	PAGE
Table of Contents . . . . .	113
Introduction . . . . .	115
Part I.—Indoor Exposure Tests, and Laboratory Experiments . . . . .	117
Part II.—Open-Air Exposure Tests . . . . .	166
Appendix . . . . .	179
Summary . . . . .	179
<i>Discussion.</i> A. E. Munby, Prof. H. C. H. Carpenter, G. D. Bengough, U. R. Evans, Prof. E. Wilson, Prof. T. Turner, R. S. Hutton, J. S. Owens, The President, Prof. R. C. Gale, Prof. A. W. Porter, A. Wolf, Prof. W. H. Merrett, S. Field, W. S. Patterson, L. H. Callendar, Prof. C. Benedicks, A. J. G. Smout, J. Newton Friend, Prof. C. O. Bannister H. Sutton, J. W. W. Willstrop . . . . .	185

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Vol. XXIII. Part 3.

MAY, 1927.

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## Contents.

	PAGE
The Problem of the Surface Tension of Mercury and the Action of Aqueous Solutions on a Mercury Surface By R. S. Burdon and M. L. Olphand. <i>(A contribution to the General Discussion on Phenomena at Interfaces)</i>	205
The Electro-deposition of Iron-nickel Alloys. Part I By S. Glasstone and T. E. Symes	213
The Decomposition of Nitrous Oxide in the Silent Electric Discharge By S. S. Joshi	227
A Recording Hydrostatic Balance of Simple Design. By F. G. Tryhorn and W. F. Wyatt	238
Investigations on Gaseous Explosions:—	
Part II. Ionisation in Detonating and Non-detonating Mixtures of Hydrogen and Oxygen. By S. W. Saunders	242
Part III. Ionisation in Explosions of Carbon Monoxide and Oxygen. By S. W. Saunders and K. Sato	248
Part IV. Ionisation in Methane-oxygen and Acetylene-oxygen Explosions. By S. W. Saunders	256
Reviews	266

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No. 76.

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FOUNDED 1903.

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## Contents.

	PAGE
The Action of Iron as an Impurity in the Lead Accumulator Part I., Capacity Loss due to Self-discharge Part II, Permanent Capacity Loss. Adsorption and Desorption of the Iron by the Positive Plate By F. M. Lea and J. T. Crennell	269
The Electrical Conductivity of Vapours and Liquid Drops during Incipient Combustion. By J. A. J. Bennett	295
The Decomposition of some Organic Substances by the Electric Spark. By N. R. Fowler and E. W. J. Mardles	301
Ionisation in Flames of Various Organic Substances By J. A. J. Bennett	307
The Law of Capillary Flow in the Case of Colloids. By Professor A. W. Porter and P. A. M. Rao	311
Note on the Soret Effect. By Professor A. W. Porter	314
The Velocity of the Decomposition of Nitroacetic Acid in Aqueous Solution By K. J. Peetersen	316
Reviews	329

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No. 77.

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*Faraday*

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AUGUST, 1927.

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## Contents.

### The Theory of Strong Electrolytes.

A General Discussion.

#### Part I.—Mobilities of Ions.

	PAGE
INTRODUCTORY PAPER. Report on Conductivity of Strong Electrolytes in Dilute Solutions. By P. Debye . . . . .	334
Report on a Revision of the Conductivity Theory. By L. Onsager . . . . .	341
<i>General Discussion.</i> H. Hartley, Prof. T. M. Lowry, Prof. A. J. Allmand, C. R. Bury, The President, C. W. Davies, Dr. L. Onsager . . . . .	349
Refractometric Evidence for the Existence of Undissociated Molecules and Complex Ions in Solutions of Strong Electrolytes. By K. Fajans . . . . .	357
<i>General Discussion.</i> Prof. J. N. Bronsted, Prof. K. Fajans, Prof. G. Hevesy, Prof. N. Bjerrum, Prof. K. Fajans, Prof. A. W. Porter, Prof. K. Fajans, F. I. G. Rawlins, Prof. K. Fajans . . . . .	375
Electrolytic Transference of Water, True Transference Numbers, Ionic Mobilities and Water Sheaths of the Ions. By H. Remy . . . . .	381
Ionic Mobilities in Non-aqueous Solvents. By H. Ulich . . . . .	388
The Mobilities of the Elementary Ions in Methyl Alcohol. By H. Hartley and H. R. Raikes . . . . .	393
Notes on the Debye-Huckel Theory. By H. Hartley and R. P. Bell . . . . .	396
The Ionisation of some typical Strong Electrolytes. By D. A. MacInnes and I. A. Cowperthwaite . . . . .	400
On the Agreement with Experiment of the Dilution Formula deduced from the Debye-Huckel Theory. By A. Ferguson and I. Vogel . . . . .	404
<i>General Discussion.</i> H. Hartley, Prof. K. Fajans, R. H. Fowler, R. T. Lattey, W. F. K. Wynne-Jones, Dr. H. Ulich, Prof. A. W. Porter, Prof. A. J. Allmand, Dr. A. Ferguson and I. Vogel, Prof. H. Remy, Dr. H. Ulich . . . . .	408

(Contents continued over the page.)

GURNEY AND JACKSON  
LONDON: 33 PATERNOSTER ROW  
EDINBURGH: TWEEDDALE COURT

# CONTENTS—continued.

## Part II.—Activity.

	PAGE
INTRODUCTORY PAPER. On the Activity of Electrolytes. By J. N. Brønsted . . . . .	416
<i>General Discussion.</i> Prof. N. Bjerrum, W. F. K. Wynne-Jones, Dr. L. Onsager, Prof. N. Bjerrum, R. H. Fowler, Prof. J. N. Brønsted	432
Strong Electrolytes in Relation to Statistical Theory, in Particular the Phase Integral of Gibbs. By R. H. Fowler . . . . .	434
Note on the Interionic Attraction Theory of Debye and Hückel. By D. L. Chapman . . . . .	443
Some Anomalies in the Theory of Solution of Strong Electrolytes and their Explanation. By N. Bjerrum . . . . .	445
Mixed Solutions of Electrolytes and Non-electrolytes. By G. Scatchard . . . . .	454
On the Thermodynamic Properties of a few Concentrated Salt Solutions. By H. S. Harned . . . . .	462
An Electrometric Study of the System Potassium Chloride—Lead Chloride—Water at 25° C. By A. J. Allmand and L. J. Burrage . . . . .	470
Note on the occurrence of Points of Inflection in the Concentration-Vapour Pressure Curves of Aqueous Solutions of certain Electrolytes. By A. J. Allmand . . . . .	477
The Activity of Zinc Chloride in Concentrated Solution. By F. Foxton and W. J. Shutt . . . . .	480
The Influence of Electrolytes on the Solubility of other Electrolytes in Non-aqueous Solvents. By C. A. Kraus and R. P. Seward . . . . .	488
The Use of Amalgam Electrodes for determining Activities in Methyl Alcohol. By J. H. Wolfenden, C. P. Wright, N. L. Ross-Kane, and P. S. Buckley . . . . .	491
The Significance of the Activity Coefficient. By Merle Randall . . . . .	498
Methods of Calculation of Activity Coefficients. By Merle Randall . . . . .	502
The Molecular Structure of Strong and Weak Electrolytes. (a) Complete Ionisation (The Electronic Theory of Valency, Part V.). By T. M. Lowry . . . . .	508
A Note on the Activity of Hydrogen Ion in Mixed Solvents. By H. Millet . . . . .	515
The Effect of One Salt on the Solubility of Another in Ethyl Alcohol Solution, Part I Part II., Quantitative Discussion of the Solubility of Sodium Iodide in the presence of Sodium Thiocyanate. By F. E. King and J. R. Partington . . . . .	522
The Activity Coefficients of Protein Ions. By G. S. Adair . . . . .	536
<i>General Discussion.</i> Prof. K. Fajans, Prof. A. W. Porter, Prof. G. Scatchard, Dr. J. A. V. Butler, Dr. J. N. Pring, Dr. H. Millet, Dr. J. A. Christiansen, Prof. G. Scatchard, Prof. J. N. Brønsted, Prof. H. S. Harned, Prof. T. M. Lowry . . . . .	538
Index . . . . .	542

No. 78.

# Transactions of the Society.

Vol. 78. 1927  
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FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY,  
CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS.

Vol. XXIII.

SEPTEMBER, 1927.

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## Contents.

	PAGE
The Thermal Decomposition of Hydrogen Peroxide Vapour. By L. W. Elder, Jr., and E. K. Rideal . . . . .	545
The Critical Potentials of Nitrogen and the Nature of Active Nitrogen By A. S. Levesley . . . . .	552
The Vapour Pressures of Diphenyl and of Aniline By F. J. Garrick . . . . .	560
A Method of Measuring Variations of Electrical Resistance for the Determination of the Thermal Equilibrium Diagram of an Inter-Metallic System. By F. H. Jeffery . . . . .	563
On the Persistence of Potential at a Mercury Cathode on Open Circuit. By F. P. Bowden, Jr. . . . .	571
On the Nature of the Activating Radiation in Photo-Chemical Action. By Wilfrid Taylor and Arthur Elliot . . . . .	583
The Effect of Series Resistance on the Current from a Photo-Active Cell containing a Fluorescent Electrolyte. By Carleton C. Murdock and Dorothy Waugh Murdock . . . . .	593
Reviews of Books . . . . .	601

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Mlle G. CAUQUIL. Solubilité de quelques gaz dans le cyclo-hexanol.  
N. de KOLOSSOWSKY. La dilatation des liquides et la chaleur de vaporisation.  
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---

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---

## Contents.

	PAGE
The Decomposition of Methyl Sulphonium Bromide in Mixed Solvents. By R. F. Corran . . . . .	605
The Structure and Formation of Colloidal Particles. By H. Freundlich . . . . .	614
Gelation of Silicic Acid. The Formation of Gas Bubbles and Drops in Silicic Acid during Gelation. By H. A. Fells and J. B. Firth . . . . .	623
Periodic Anomalies in the Properties of Long Chain Compounds. By W. B. Lee . . . . .	634
The Electrolytic Oxidation of <i>p</i> -Toluic Acid in Alkaline Solution. By A. J. Allmand and A. Puttick . . . . .	643
Hydrolysis of the Peptide (—CO—NH—) Linkage. By A. I. Escolme and W. C. M. Lewis . . . . .	654
A New Method of Measuring Overvoltage. By L. J. P. Byrne . . . . .	660
The Free Energy of Transition in the System Calcite-Aragonite. By J. L. Buchan . . . . .	666
The Free Energies of Solid Compounds Deduced from their Crystal Structure: with Special Reference to Calcite and Aragonite. By J. L. Buchan . . . . .	672
Reviews of Books. . . . .	677
Index of Volume XXIII . . . . .	682

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VOL. XXIII.

JANUARY, 1927.

PART I.

## VAPOUR PRESSURE AND HEAT OF DILUTION OF AQUEOUS SOLUTIONS.

### PART II.

By W. R. HARRISON, PH.D. AND E. P. PERMAN, D.Sc.

*Received 18th October, 1926.*

#### A. VAPOUR PRESSURE OF AQUEOUS SOLUTIONS OF CALCIUM CHLORIDE.

Comparatively little work has been done on concentrated solutions except at low temperatures, but the following investigations should be mentioned. Wade<sup>1</sup> made determinations of the boiling-points of concentrated aqueous solutions at various pressures and hence determined their vapour pressures. Lord Berkeley worked with solutions of cane sugar and calcium ferrocyanide at temperatures up to 30° C. More recent work is that of Perman and Price,<sup>2</sup> D. O. Wood,<sup>3</sup> Perman and Saunders,<sup>4</sup> Perman and Lovett.<sup>5</sup> In America, Frazer and Lovelace<sup>6</sup> using a static method, and Washburn and Heuse<sup>7</sup> with a dynamic method, have made very accurate vapour pressure measurements of concentrated aqueous solutions, but over a very limited range of low temperatures.

#### Method of Vapour Pressure Measurement.

The method used by us was a modification of that of Perman and Saunders; it enabled a number of measurements at different concentrations to be made with only one filling of the flask containing the solution. In the modified form (see Fig. 1) the capillary tube was connected by a ground glass joint to a horizontal tube which was sealed to a vertical helix leading to the top of a bulb of about 30 c.c. capacity. A vertical tube which passed up the centre of the helix, joined this bulb to a wide tube containing phosphorus pentoxide. The wide tube was closed with a ground glass

<sup>1</sup> *Proc. Roy. Soc.*, 1895.

<sup>3</sup> *Ibid.*, 1915.

<sup>6</sup> *J. Amer. Chem. Soc.*, 1914, 1920.

<sup>2</sup> *Trans. Far. Soc.*, 1912.

<sup>4</sup> *Ibid.*, 1923.

<sup>7</sup> *Ibid.*, 1914.

<sup>5</sup> *Ibid.*, 1926.

stopper, and this served as a tap between the wide tube and the narrow side tube which was sealed to it. This side tube was connected through another ground joint with two U-tubes containing phosphorus pentoxide; both U-tubes were provided with stopper stop-cocks and ground joints on their side tubes. The second U-tube was connected to a small mercury vacuum gauge and a vacuum pump. To use this apparatus, the whole of the condensation system was evacuated to a pressure of a few mm. and then the stop-cock between the condensation bulb and its guard tube was closed. The bulb and helix were immersed in cold water and, when the stop-cock at the top of the solution bulb was opened, the solvent distilled over, was condensed in the helix and collected in the bulb. The rapid distillation removed all air from the vapour pressure apparatus; the air collected above the water in the condensation bulb and was pumped off from time to time by opening the stop-cock communicating with the guard tube.

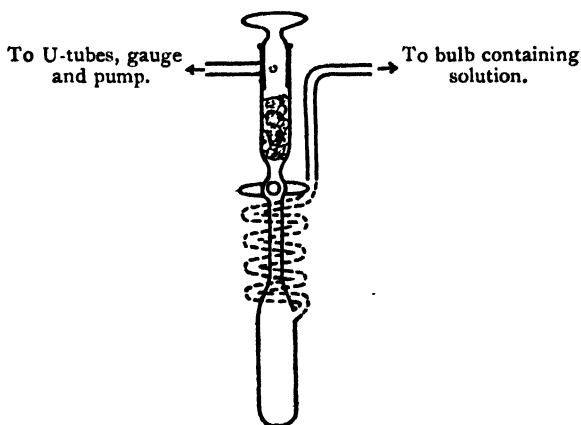


FIG. 1.—Absorption tube.

The condensation apparatus was of a form which is easily weighed and, knowing the original amounts of solute and solvent in the apparatus, successive quantities of solvent could be distilled off and weighed, thus varying the concentration of the solution in the flask by any desired amount. Once the air had been removed by the initial distillation, very small successive quantities of solvent could be removed with the assurance that the solutions were air free. It was found that practically all the solvent removed from the apparatus was retained by the condensation apparatus, the first U-tube following it rarely gaining as much as a milligram in weight, but as a matter of precaution, this U-tube was always weighed, as was the second, at the close of a series.

No lubricant was used on the joints—they were simply pressed together and then covered with rubber tubing. The stop-cock at the top of the neck of the solution bulb was lubricated with a special high temperature lubricant.

The calcium chloride, purchased as the hexahydrate, was recrystallised for the vapour pressure determinations and was then proved to be free from insoluble matter, barium, strontium, heavy metals, phosphates, and alkalis. Owing to the deliquescent nature of calcium chloride, and to avoid a troublesome determination for each series of vapour pressures, a concentrated stock solution was made up. This was very accurately

standardised (a) volumetrically against silver nitrate, (b) by evaporating a weighed quantity of the solution in an air oven whose temperature was gradually raised to 175° C. and maintained there until the weight of the residual anhydrous calcium chloride was constant. Although tested regularly, and ultimately at the end of a year, the concentration of the stock solution was not found to alter appreciably. The same stock solution was used throughout.

### Experimental Procedure.

The first measurement was made in the same way as described by Perman and Saunders (*loc. cit.*), but further measurements were greatly facilitated by the condensation apparatus. By its use a whole series of vapour pressures was obtained for each initial solution; the amounts of solvent removed at each distillation could be made very small, and so the vapour pressure-concentration curve of an aqueous solution could be followed extremely closely. When there remained but about 35 c.c. of solution, the apparatus was taken out of the thermostat, cooled, dried and weighed; this constituted a check upon the amounts of solvent removed and weighed in the condensation apparatus.

In working along a vapour pressure-concentration curve at any temperature, it was generally arranged that each portion of the curve was covered by the beginning of one series, the middle of another and the end of a third. In this way, risk of error was minimised and a valuable check obtained on the completeness of the removal of air.

Experiments were carried out in order to find the minimum quantity of solvent to be distilled off initially so as to render the pressure of the residual air, if any, less than the limit of error due to other causes. The apparatus having been filled with water in the usual way, 3 c.c. of water were distilled off and the vapour pressure of the residual water was measured and found to be slightly too high. A further 4 c.c. were removed and then the measured vapour pressure was found to be correct, showing that the distillation of but 7 c.c. of water was effective in removing all detectable traces of air from the solution and apparatus.

However, as a precaution, never less than 30 c.c. of solvents corresponding to about one hundred litres of water vapour under the conditions of experiment, were distilled off at the beginning of each series of determinations. To facilitate the work, the distillation process was carried on in a separate bath which was kept nearly boiling.

The results of the vapour pressure measurements are given in Table I. The densities of calcium chloride solutions are given in Table II.

The concentration of the solutions is expressed in three ways:—

as  $n/N$ , this being the ratio of solute to solvent molecules;

as  $C_2$ , which is the number of grammes of the anhydrous solute contained in a hundred grammes of solution;

as  $C_3$ , which is the number of grammes of the anhydrous solute contained in a litre of solution at the temperature of the experiment. For this, the density of the solution is required and this is given under the heading D.

The vapour pressures are given in millimetres of mercury measured at 0° C.

## VAPOUR PRESSURE AND AQUEOUS SOLUTIONS

TABLE I.—VAPOUR PRESSURES OF CALCIUM CHLORIDE SOLUTIONS.

Temp.	n/N.	C <sub>2</sub> .	D.	C <sub>3</sub> .	Vapour Pressure.
40°00° C.	0	0	—	0	55°2
	0°0036	2°26	1°014	22°9	55°1
	0°0059	2°92	1°018	29°7	55°0
	0°0068	4°01	1°031	41°3	54°9
	0°0116	6°69	1°050	70°2	54°6
	0°0180	10°01	1°092	109°3	52°2
	0°0233	12°57	1°116	140°3	52°0
	0°0279	14°66	1°133	166°1	50°4
	0°0315	16°27	1°154	187°8	49°7
	0°0382	19°10	1°179	225°2	48°2
	0°0419	20°52	1°196	245°4	46°5
	0°0488	23°15	1°220	282°4	45°5
	0°0620	27°66	1°265	349°9	40°2
	0°0791	32°79	1°319	432°5	34°7
	0°1015	38°5	1°383	532°0	27°8
	0°1311	44°7	1°452	649°0	20°7
	0°1681	50°9	1°520	773°0	13°9
	0°2267	56°3	1°580	889°0	11°1
50°00° C.	0	0	—	0	92°4
	0°0052	3°10	1°016	31°49	90°4
	0°0092	5°50	1°040	57°21	90°2
	0°0133	7°58	1°060	80°3	88°9
	0°0161	9°01	1°073	96°7	88°5
	0°0213	11°59	1°096	127°3	86°8
	0°0236	12°72	1°104	140°4	86°2
	0°0263	13°94	1°117	155°6	85°7
	0°0315	16°24	1°139	184°9	83°0
	0°0381	19°00	1°164	221°2	80°4
	0°0475	22°66	1°204	272°8	75°3
	0°0641	28°32	1°252	354°6	66°3
	0°0695	29°01	1°256	364°3	65°0
	0°0832	33°90	1°300	440°7	55°4
	0°0936	36°6	1°329	486°3	48°6
	0°1150	41°5	1°380	572°7	38°4
	0°1404	46°4	1°438	667°2	30°5
	0°1716	51°4	1°500	771°0	22°7
	0°2089	56°3	1°564	880°5	16°3
60°00° C.	0	0	—	0	149°3
	0°0032	1°94	°997	19°8	149°3
	0°0033	2°25	°999	22°5	149°2
	0°0053	3°18	1°006	32°0	143°7
	0°0096	5°51	1°026	56°4	146°8
	0°0113	6°48	1°034	67°0	145°7
	0°0118	6°69	1°038	69°4	145°0
	0°0130	7°38	1°042	76°9	144°0
	0°0138	10°36	1°067	110°5	141°3
	0°0228	12°38	1°084	134°2	139°5
	0°0390	19°93	1°104	220°0	129°0
	0°0462	22°09	1°171	258°7	124°0
	0°0504	23°70	1°188	281°9	119°3
	0°0577	26°24	1°215	318°8	112°8
	0°0634	28°10	1°244	349°5	108°9
	0°0708	30°40	1°258	382°4	100°3
	0°0777	32°40	1°280	414°7	94°8
	0°0854	36°45	1°321	481°9	81°5
	0°1248	43°50	1°395	606°8	59°6
	0°1477	47°66	1°439	686°3	48°0
	0°1745	51°86	1°474	764°3	38°4
	0°2072	56°1	1°529	858°0	28°7

TABLE I.—*Continued.*

Temp.	$n/N$ .	C <sub>2</sub> .	D.	C <sub>3</sub> .	Vapour Pressure.
70°00° C.	0	0	—	0	233·8
	0·0057	3·39	1·004	34·0	233·0
	0·0103	5·75	1·024	58·7	228·0
	0·0134	7·61	1·040	79·1	226·3
	0·0143	8·08	1·044	84·3	227·0
	0·0182	10·11	1·062	107·4	222·8
	0·0240	12·92	1·087	140·3	217·2
	0·0307	15·85	1·116	176·9	211·4
	0·0393	19·81	1·156	218·9	201·7
	0·0616	24·13	1·195	288·2	186·8
	0·0562	25·74	1·200	311·5	181·2
	0·0607	27·22	1·225	333·8	175·6
	0·0706	30·36	1·260	362·5	160·5
	0·0894	35·54	1·316	467·7	134·0
	0·0960	37·18	1·334	495·8	125·0
	0·1120	40·86	1·385	565·8	107·2
	0·1279	44·10	1·407	620·5	94·0
	0·1519	48·36	1·455	703·6	76·5
	0·1770	52·19	1·494	780·6	60·0
	0·2134	56·82	1·546	878·4	43·2
	0·2233	57·92	1·556	901·2	42·1
80°00° C.	0	0	—	0	55·4
	0·0041	2·48	·994	24·7	352·1
	0·0048	2·93	·998	29·3	351·8
	0·0060	3·61	1·003	36·1	351·0
	0·0100	5·73	1·120	58·4	346·2
	0·0104	5·87	1·022	60·0	346·0
	0·0144	8·15	1·042	86·4	342·9
	0·0233	11·60	1·070	124·0	334·6
	0·0268	14·13	1·090	154·1	328·8
	0·0297	15·40	1·102	169·7	323·7
	0·0364	18·17	1·124	204·2	316·0
	0·0411	20·20	1·142	230·7	304·1
	0·0475	22·55	1·162	262·0	295·2
	0·0516	24·07	1·178	283·5	287·6
	0·0626	27·82	1·218	338·7	264·4
	0·0741	31·30	1·257	393·2	240·9
	0·0939	37·08	1·320	489·4	198·9
	0·1117	40·81	1·363	556·2	170·6
	0·1312	44·48	1·400	622·7	143·4
	0·1599	49·70	1·460	726·0	112·8
	0·1833	52·96	1·496	792·2	96·4
	0·2176	57·32	1·546	886·1	75·5
	0·2491	60·5	1·583	957·0	63·2

In order to show the general trend of the vapour pressure curves, they are given in Fig. 2. The most noteworthy point is the double flexure shown by each curve. This distinguishes the curves from those obtained for urea solutions. Both urea and calcium chloride are very soluble, but the latter forms hydrates, and ionises in solution, whilst the former does not. We would suggest therefore that the flexure at the higher concentrations is due to decrease of ionisation, or decrease of hydration, or to both of these effects. By hydration we do not necessarily imply the formation of definite hydrates.

TABLE II.—THE DENSITIES OF CALCIUM CHLORIDE SOLUTIONS.

Temperature.	Per Cent. CaCl <sub>2</sub> .	n/N.	Density in Gm./c.c.
40°00° C.	0	0	0·992
	7·01	0·0120	1·107
	14·71	0·0280	1·134
	18·93	0·0379	1·174
	32·40	0·0774	1·311
	37·80	0·0986	1·387
	48·51	0·1528	1·496
	56·3	0·2089	1·586
50°00° C.	0	0	0·988
	4·96	0·0085	1·038
	10·87	0·0198	1·090
	15·84	0·0305	1·285
	22·01	0·0458	1·187
	26·09	0·0573	1·226
	32·40	0·0774	1·285
	40·60	0·1108	1·365
	50·27	0·1636	1·496
	56·30	0·2089	1·564
60°00° C.	0	0	0·983
	3·23	0·0054	1·002
	4·14	0·0070	1·016
	11·35	0·0208	1·119
	16·49	0·0320	1·077
	20·66	0·0422	1·160
	24·62	0·0530	1·200
	32·40	0·0774	1·280
	42·60	0·1203	1·388
	51·9	0·1750	1·480
70°00° C.	0	0	0·977
	3·38	0·0057	1·002
	4·66	0·0079	1·015
	10·88	0·0198	1·066
	14·30	0·0271	1·100
	21·44	0·0443	1·169
	27·38	0·0612	1·228
	32·79	0·0791	1·288
	34·27	0·0946	1·308
	36·66	0·0939	1·333
	42·09	0·1179	1·387
	49·25	0·1574	1·480
	50·96	0·1685	1·494
	58·01	0·2241	1·530
80°00° C.	0	0	0·972
	9·70	0·0174	1·058
	11·25	0·0206	1·063
	21·80	0·0452	1·162
	32·30	0·0774	1·207
	43·00	0·1223	1·384
	56·41	0·2095	1·538

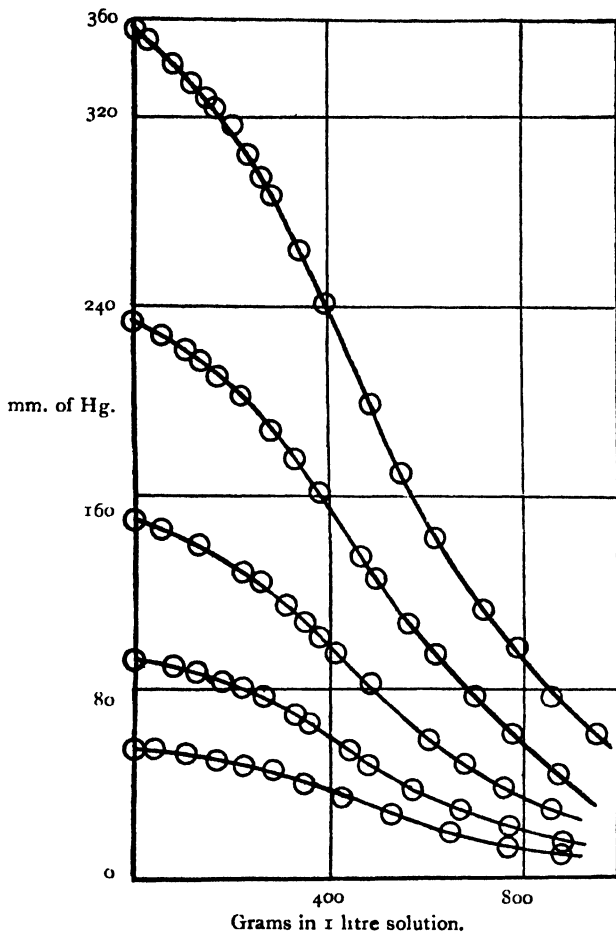


FIG. 2.—Vapour-pressure of calcium chloride solution.

### B. THE HEAT OF DILUTION OF CONCENTRATED SOLUTION OF CALCIUM CHLORIDE.

A short account of previous work is given by Perman and Lovett.<sup>1</sup> These investigators used Tucker's form of dilution apparatus, but improved the accuracy of the measurements by using a mercury thermometer as a null point instrument, and measuring the heat evolved electrically, and introduced modifications which allowed measurements to be made over a range of temperature.

Whilst this method had the merit of simplicity it could be applied only to the study of those solutions which absorbed heat on being diluted and, for the more accurate work necessary for measurements on solutions with extremely small heats of dilution, it was necessary to make some radical changes in the form of apparatus employed.

The experimental solution was contained, and the heat changes were effected, in a silvered Dewar flask, which was about 28 cm. deep, of 3 cm. radius, and had a capacity of about 700 c.c. The flask was fitted with a

<sup>1</sup> *Trans. Far. Soc.*, Vol. XXII.

tightly fitting rubber bung, 4 cm. thick, through which were bored six holes. Through the central hole passed a glass tube 10 cm. long which acted as a bearing for the shaft of a glass screw blade stirrer; through another hole passed a glass tube into which a Beckmann thermometer fitted tightly, so that its bulb was just above the blade of the stirrer. A tube of thin glass, about 6 mm. diameter, sealed at the lower end passed through the third hole and just dipped into the solution; this was called the cooling tube and its use will be referred to in the account of the experimental procedure. A glass tube about 1 cm. in diameter and 8 cm. in length, passed through another hole. This tube was kept closed by a tightly fitting long rubber stopper and was used for the introduction of the experimental solution and the removal of some of the diluted solution by means of a special pipette. The glass outer case of the heating coil passed through the fifth hole in the bung.

The apparatus was designed, and the experimental procedure was so arranged, that no account need be taken of the lag in the delivery of heat from the coil to the solution; a simple form of heating coil could therefore be used. The heating coil itself was made of bare Chromalloy IV. resistance wire, 30 gauge, which has a resistance of 6 ohms. to the foot. About ten to eleven inches of the wire were coiled into a helix about two inches long and a quarter of an inch in diameter. It was fitted into a thin glass tube in the way described by Perman and Lovett. Compared with the resistance of the actual coil, that of the two thick copper supporting leads which were kept sprung apart in the tube, was negligible.

Through the sixth hole, which was bored near the edge of the bung, passed the side tube of the external dilution vessel; this was a cylindrical glass vessel of about 7 cm. diameter and had a capacity of about a litre and a half. A horizontal side tube was sealed on near the top, and to the end of this was sealed a vertical capillary tube 18 cm. long with a bore of 1 mm. This vertical side tube passed through the bung and then dipped deeply into the solution in the Dewar flask. A vertical tube was sealed through the top of the dilution vessel: this tube reached nearly to the bottom. Its upper portion was capillary and passed through a stop-cock before spreading out to form one portion of a ground glass joint.

The second portion of the dilution vessel, henceforth termed the dilution pipette, was a cylindrical glass vessel of about 35 c.c. capacity, closed at both ends by capillary stopcocks. One end of this pipette was made to fit into the end of the vertical tube of the dilution vessel. Water which was to be added to the experimental solution was heated and weighed in this vessel. The dilution vessel and the capillary side tube were kept filled with water and, when it was required to introduce a weighed amount of water into the solution, the pipette was filled with water, weighed, heated to the correct temperature and, then, fitted to the dilution vessel. On opening the three taps, gravity caused the water in the pipette to enter the vertical tube which delivered it to the bottom of the dilution vessel, from which it expelled an equal volume of water from the top, through the side tube into the Dewar flask.

The dilution pipette and contained water were heated by hanging the pipette inside a wide glass tube which had been covered with a layer of asbestos on which was wound many turns of resistance wire. This tube was fitted inside a non-conducting case and the coil was connected through a variable resistance to the electric mains. The tube was closed with a wooden cover through which projected a thermometer. By varying the current, the interior of the tube could be maintained at any desired temperature.

The water from the pipette was generally a degree or so cooler than that in the dilution vessel and so remained at the bottom, whilst owing to the small coefficient of expansion of water, a practically equal weight of water from the top of the vessel, and therefore at the correct temperature, was delivered into the Dewar flask. When sufficient water had been added, the taps were closed and the dilution pipette, containing the remaining water, was removed and dried before being weighed to find the amount of water which had been transferred to the Dewar flask.

To maintain the Dewar flask and dilution vessel at the correct temperature, both were immersed in a thermostat. This consisted of a well-lagged copper tank,  $30 \times 30 \times 50$  cm. and was electrically heated and controlled. The water in the tank was covered by a cm. layer of liquid paraffin which so materially reduced evaporation, that there was no need to fit a constant water level device.

At first radiator lamps were employed as the main heaters, but as these proved fragile, they were replaced by coils of resistance wire housed in brass tubes which were filled with transformer oil. These heaters were placed vertically in the tank, which was thus heated fairly evenly. The heaters were connected to the mains and were so arranged, in series and in parallel, that they supplied not quite enough heat to maintain the bath at the required temperature.

The thermostat was regulated by a small electric lamp which was fixed in the centre of the tank. As most of its heat was supplied by radiation, it heated the water quite uniformly, and had practically no lag. A toluene regulator with an electric control was employed. By using a long tube (3 metres by 1 cm.) running round the thermostat, the temperature was maintained constant to  $0.01^\circ$  C. Sparking was obviated by connecting a condenser of large capacity—two  $\mu F$ —across the gap.

Thorough stirring was effected by having four shafts, one in each corner of the bath, mounted on ball bearings. Each shaft was fitted with two sets of four screw propeller blades, one set near the top and the other near the bottom. The whole was driven by a hot air engine. The Dewar flask and dilution vessel were fitted in such a position that there was a depth of about 5 cm. of water over the top of the rubber bung.

At each temperature, the speed of stirring was so arranged that the heat developed by the stirring was exactly equal to that lost by conduction along the leads of the heating coil, so that no estimation of, nor allowance for the amount of heat generated by the stirrer was necessary.

The circuit of the electrical system used for the measurement of the heat of dilution is shown in Fig. 3.

To determine the heat generated in the coil, the potential difference at its terminals and also the potential difference across a standard ohm placed in series with the coil were measured by the potentiometer whilst a steady current was being passed through the coil and the standard ohm.

Included in the main heating circuit, was a fixed resistance of about 1 ohm which was shunted by a variable resistance of 350 ohms. This resistance was varied by means of a wheel and screw arrangement which made fine and rapid adjustment very simple and convenient. In the circuit shown in Fig. 3, the main heating circuit is shown in continuous and the connections to the potentiometer in dotted lines.

The whole of the apparatus was enclosed in a cubicle, the air of which was maintained at a constant temperature of  $17^\circ$  C. by means of a regulator and an electric heater.

**Experimental Procedure.**

The two Beckmann thermometers were set conveniently and were then allowed to remain in the thermostat for at least twenty-four hours, so that their bulbs might become free from strain. They were then carefully compared with each other and with the standard thermometer, care being taken to give the same depth of immersion as that suffered later by one of them inside the Dewar flask. Corrections for the exposed stem were applied, so that those readings of the thermometers which corresponded to the temperature of the thermostat, could be determined to the nearest thousandth of a degree.

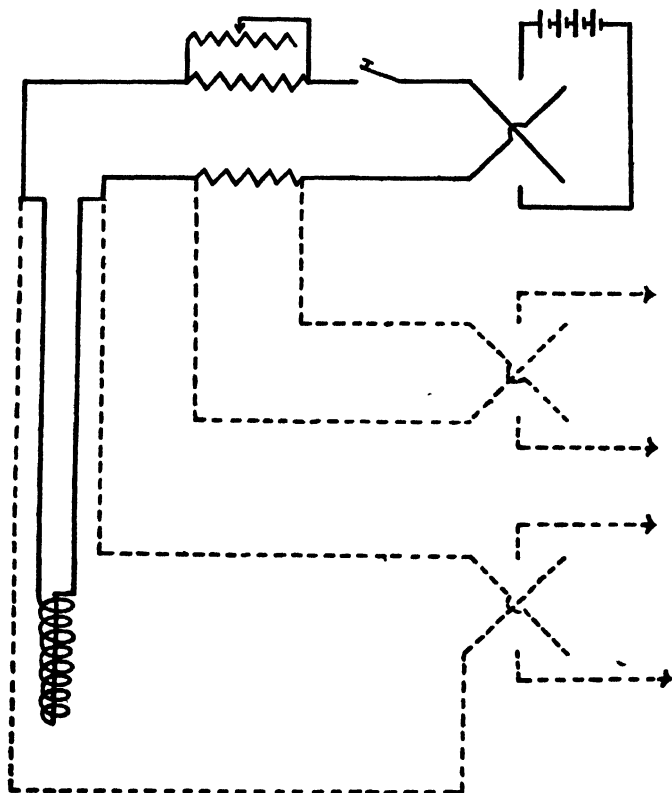


FIG. 3.

The thermostat having been set, the dilution vessel and the side tube were completely filled with cold distilled water which had been rendered air free by long boiling. The side tube of the dilution vessel was then fitted through the bung of the Dewar flask and the whole fixed in the clamps of the stand inside the thermostat.

The warming of the water in the dilution vessel caused the escape of a small quantity into the flask; this however ceased when the water in the dilution vessel had attained the temperature of the thermostat. When this was the case, the water in the Dewar flask was sucked out and the last traces of moisture were removed by drawing air through it.

The experimental solution was made up and, after having been heated to slightly above the correct temperature, was weighed in a stoppered bottle.

This solution was poured into the flask by means of the short wide tube passing through the bung.

The bottle was reweighed to find the weight of solution added. For calcium chloride, a solution which was nearly saturated was used.

The stirrer was set in motion and the Beckmann thermometer fitted into its sheath. When the solution had attained a steady temperature, it was, if necessary, heated by means of the coil until it was at the correct temperature—that of the water in the thermostat outside. If the solution was at too high a temperature, it was cooled by pouring a little ether into the cooling tube into which was blown a current of air from a water blower. When sufficient cooling had been effected, the air-pipe was removed, the excess ether sucked out and the last traces removed by a minute's further blowing. Generally, the solution was over-cooled and then brought up to the correct temperature by means of the heating coil.

When this adjustment had been made, the solution was stirred and the Beckmann thermometer was observed over a period of two hours in order to detect any change in temperature which would show that this balance had not been effected.

The accumulators, which provided the steady fall of potential in the internal circuit of the potentiometer, were connected to the instrument and allowed to deliver current for a few hours before the experiment, so that they could have an opportunity of settling into a steady state. When this had been done, one of the standard cells was thrown into the circuit and the potentiometer rheostat was adjusted until no deflection of the galvanometer was observed on making the correct contact. The potentiometer was thus set to give direct readings of potential.

The dilution was then carried out by running in water from the dilution vessel, the loss of weight giving the amount added.

The Beckmann thermometer was used purely as a qualitative instrument, so that there was no need to calibrate its thread. For each determination, two points on its scale were observed, one, which was fixed throughout the series—corresponding to the temperature of the thermostat—and the other, the temperature to which the solution changed consequent upon the addition of the dilution water. Both of these points were observed on a stationary mercury thread and were, consequently, determined with a maximum of accuracy.

After the dilution and observation of the new position of the mercury thread of the thermometer, the solution was cooled below the lower of the two points. The heating coil was then switched on and, after a short time, the potentiometer switches were turned so as to indicate the potential difference across the terminals of the heating coil and, the balance once obtained, the spring contact was kept pressed down. Any variation in the current—shown by a deflection of the galvanometer needle—was immediately corrected by turning the wheel of the variable resistance.

When the thread was approaching the lower point, the stem of the thermometer was tapped to prevent sticking and, the moment the thread reached the point, the release of a stop-watch was pressed. The galvanometer was watched and the current kept constant by means of the rheostat, until about half of the heating had been done. The commutator rocker was pushed over and the potentiometer rapidly readjusted.

Owing to the care taken in soldering the coil and in making the connections, the thermo-electromotive forces were found to be practically negligible, being of the order of a ten thousandth of a volt.

At the second observed point on the scale, the procedure was similar.

The potentiometer switches were turned so as to indicate the potential difference across the terminals of the standard ohm, and then the heating current was switched off.

The solution was cooled and the procedure repeated. The temperature of the oil surrounding the standard ohm was taken at the beginning and end of heating.

The change of temperature due to the dilution, was usually of the order of a fifth of a degree. The following assumptions are involved in the above procedure:—

(1) That there was no error due to diffusion of the solute into the diluting water through the capillary side tube. The side tube was very long and of quite a fine bore, especially at the end.

(2) That the heating coil was supplying heat to the solution at a steady rate. Separate experiments on the rate of rise of temperature as shown by the Beckmann thermometer, proved that once the coil had settled down, the increase of temperature was exactly proportional to the time of heating.

(3) That there was no change in the rate of heat loss from the Dewar flask and its contents due to the small change of temperature experienced by the solution due to the dilution. This follows from (2).

(4) That the lag in the reading of the thermometer was the same at both the observed temperatures.

This last assumption was tested by making several experiments, using different rates of heating between two fixed temperatures. This resulted in giving widely varying lags to the thermometer, but all the experiments gave values for the heat which were identical within the limits of experimental error.

Several sets of observations of the time of heating for each dilution experiment were made and the average was taken.

When the determination had been completed for one concentration, a quantity of the solution was removed by means of the removal pipette. This was a bulb of thin glass to which were sealed two tubes; one at the top was short and the other which was at the bottom was long enough to reach nearly to the bottom of the Dewar flask. To the lower end of this tube was fitted a ground glass cap. Solution removed from the flask could be weighed directly in this pipette.

A weighed quantity of water was poured into the flask so that the solution was brought up to its original volume. This new solution was brought to the correct temperature, and a fresh determination made as described above.

Knowing the original quantities of solute and solvent, together with the quantities of water added and solution removed, the average concentration of any solution could easily be calculated. Proceeding in this way, the heat of dilution-concentration curve of the various solutions could be determined.

The results are expressed in Table III.

The concentration of the solution is expressed in three ways:—

$C$  is the weight of the solute in 100 gms. of the solution.

$n/N$  the ratio of solute to solvent molecules.

$N/n$  the ratio of solvent to solute molecules.

The heat is expressed as the number of calories evolved on the addition of one gramme of water to an infinite quantity of solution.

The sign + or – placed before the figure for the heat, is used with the thermodynamical significance.

TABLE III.—HEATS OF DILUTION OF CALCIUM CHLORIDE SOLUTIONS.

Temp.	C	n /N.	N/n.	Heat.
40°00° C.	51'85	0'1788	5'731	-77'13
	51'31	0'1709	5'851	-75'39
	50'87	0'1677	5'963	-73'31
	50'47	0'1646	6'076	-71'20
	44'56	0'1304	7'667	-47'03
	40'20	0'1091	9'165	-32'38
	35'23	0'0886	11'29	-18'32
	30'52	0'0715	13'99	-9'74
	24'94	0'0540	18'52	-4'57
	24'26	0'0522	19'16	-4'46
	19'24	0'0388	25'77	-2'20
	14'92	0'0288	34'72	-1'12
	9'20	0'0164	60'98	-0'67
50°00° C.	50'56	0'1657	6'035	-77'64
	47'60	0'1469	6'808	-65'43
	40'67	0'1106	9'039	-35'48
	34'47	0'0844	11'85	-20'65
	29'34	0'0673	14'86	-10'66
	24'31	0'0522	19'16	-5'62
	19'46	0'0393	25'45	-2'70
	15'53	0'0402	33'11	-1'61
	11'55	0'0212	47'17	-0'85
60°00° C.	54'03	0'1920	5'208	-100'5
	48'86	0'1547	6'465	-78'21
	42'11	0'1179	8'483	-49'08
	41'70	0'1160	8'621	-46'55
	32'85	0'0795	12'58	-17'29
	26'17	0'0577	17'33	-6'49
	20'20	0'0410	24'39	-2'97
	15'30	0'0295	33'90	-1'65
	11'03	0'0203	49'26	-0'60
70°00° C.	49'61	0'1587	6'302	-81'20
	46'77	0'1425	7'018	-69'79
	37'68	0'0986	10'14	-35'07
	31'11	0'0731	13'68	-13'79
	24'21	0'0519	19'27	-6'65
	18'16	0'0362	27'62	-3'13
	12'28	0'0226	44'25	-1'10
80°00° C.	49'48	0'1578	6'337	-92'51
	46'43	0'1402	7'133	-73'43
	38'20	0'1002	9'983	-41'07
	35'65	0'0901	11'10	-29'71
	33'29	0'0810	12'35	-23'41
	26'68	0'0594	16'04	-10'85
	23'24	0'0494	20'24	-6'41
	17'99	0'0358	27'93	-3'45
	13'10	0'0242	41'32	-1'48

The Heat of Dilution—Concentration curves are nearly straight at the higher concentrations, then bend sharply and run together at the lower strengths.

Heat of Dilution has also been plotted against temperature; straight lines result up to 40 per cent. concentration and, above this, the curves are slightly convex above.

## 14 VAPOUR PRESSURE AND AQUEOUS SOLUTIONS

TABLE IV.—VAPOUR PRESSURES OF POTASSIUM CHLORIDE SOLUTIONS.

Temp.	n/N.	C <sub>2</sub> .	D.	C <sub>1</sub> .	Vapour Pressure.
40°00° C.	0	0	—	0	55·2
	0·0079	3·16	1·016	32·1	55·0
	0·0098	3·90	1·018	39·7	54·9
	0·0149	5·82	1·031	60·0	54·8
	0·0230	8·68	1·049	91·1	53·6
	0·0260	9·77	1·054	102·9	53·1
	0·0281	10·43	1·058	110·3	52·9
	0·0362	13·03	1·077	140·3	51·7
	0·0525	17·84	1·112	198·5	50·3
	0·0559	18·80	1·118	210·1	50·1
	0·0687	22·13	1·140	252·2	48·2
	0·0783	23·41	1·151	269·4	48·4
	0·0907	27·30	1·178	321·6	47·0
	0·1008	29·44	1·195	351·7	46·1
50°00° C.	0	0	—	0	92·4
	0·0107	4·23	1·014	42·9	90·1
	0·0233	8·81	1·044	92·0	89·1
	0·0296	10·91	1·058	115·4	87·6
	0·0402	14·27	1·080	154·1	86·3
	0·0660	21·46	1·133	243·1	81·7
	0·0863	26·32	1·167	307·1	77·9
	0·1035	30·00	1·194	358·2	74·7
60°00° C.	0	0	—	0	149·3
	0·0095	3·80	1·006	38·0	147·1
	0·0131	5·15	1·014	52·2	146·4
	0·0212	8·08	1·032	83·4	144·3
	0·0296	10·91	1·053	114·9	142·1
	0·0370	13·27	1·067	141·6	139·8
	0·0458	15·92	1·086	173·2	137·0
	0·0666	21·61	1·127	243·5	131·4
	0·0790	24·64	1·148	282·7	128·4
	0·0984	28·00	1·174	328·7	123·7
	0·1101	31·30	1·197	374·6	120·3
70°00° C.	0	0	—	0	233·8
	0·0109	4·14	1·002	41·4	230·2
	0·0150	5·85	1·012	59·2	229·5
	0·0186	7·16	1·021	73·1	228·6
	0·0224	8·74	1·028	87·0	226·4
	0·0287	10·18	1·039	105·7	224·4
	0·0341	12·35	1·053	130·1	221·2
	0·0382	13·66	1·061	146·1	219·3
	0·0499	17·11	1·086	185·8	214·4
	0·0676	21·92	1·123	246·1	205·6
	0·0894	27·00	1·137	307·0	195·0
	0·0957	28·38	1·148	325·7	190·8
	0·1169	32·60	1·200	391·2	184·6
80°00° C.	0	0	—	0	355·4
	0·0252	9·45	1·031	97·4	341·6
	0·0313	11·47	1·041	119·4	338·1
	0·0431	15·13	1·068	161·6	330·5
	0·0552	18·59	1·094	203·3	322·3
	0·0711	22·73	1·124	255·4	311·3
	0·0904	27·24	1·157	315·1	297·2
	0·1036	30·01	1·177	353·2	289·1
	0·1245	34·00	1·215	413·1	277·4

## PART III.

*A. VAPOUR PRESSURE OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.*

Similar methods were used for solutions of potassium chloride. The solutions were made up directly from Kahlbaum's pure salt. The results of the vapour pressure measurements are given in table IV.

TABLE V.—DENSITIES OF POTASSIUM CHLORIDE SOLUTIONS.

Temp.	Per Cent. KCl.	n/N.	Density in Gms./c.c.
40°00° C.	0	0	0'922
	3'20	0'00799	1'014
	6'93	0'01799	1'035
	10'51	0'02837	1'059
	13'91	0'03903	1'082
	16'71	0'04849	1'102
	20'67	0'06295	1'129
	23'94	0'076070	1'154
50°00° C.	0	0	0'989
	3'20	0'00799	1'009
	6'93	0'01799	1'031
	10'51	0'02837	1'055
	13'91	0'03903	1'078
	16'71	0'04849	1'097
	20'67	0'06295	1'122
	23'94	0'07607	1'149
60°00° C.	0	0	0'983
	3'20	0'00799	1'002
	6'93	0'01799	1'025
	10'51	0'02837	1'048
	13'91	0'03903	1'071
	16'71	0'04849	1'091
	20'57	0'06295	1'118
	23'94	0'07607	1'143
70°00° C.	0	0	0'977
	3'20	0'00799	0'998
	6'93	0'01799	1'019
	10'51	0'02837	1'041
	13'91	0'03903	1'064
	16'71	0'04849	1'085
	20'67	0'06295	1'110
	23'94	0'07607	1'137
80°00° C.	0	0	0'972
	3'77	0'0095	0'996
	6'96	0'0181	1'015
	9'30	0'0248	1'030
	14'42	0'0407	1'064
	19'37	0'0592	1'098
	25'02	0'0806	1'138

The vapour pressure curves (not reproduced here), vapour pressure as ordinates and volume concentration as abscissæ, are not far from straight, but are slightly convex upwards. As the solubility is much less than that of calcium chloride, the vapour pressures cover a much smaller range. The densities are given as well.

*B. HEAT OF DILUTION OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.*

The method used for measuring the heat of dilution was the same as described in Part II., but owing to the very small heat change involved the

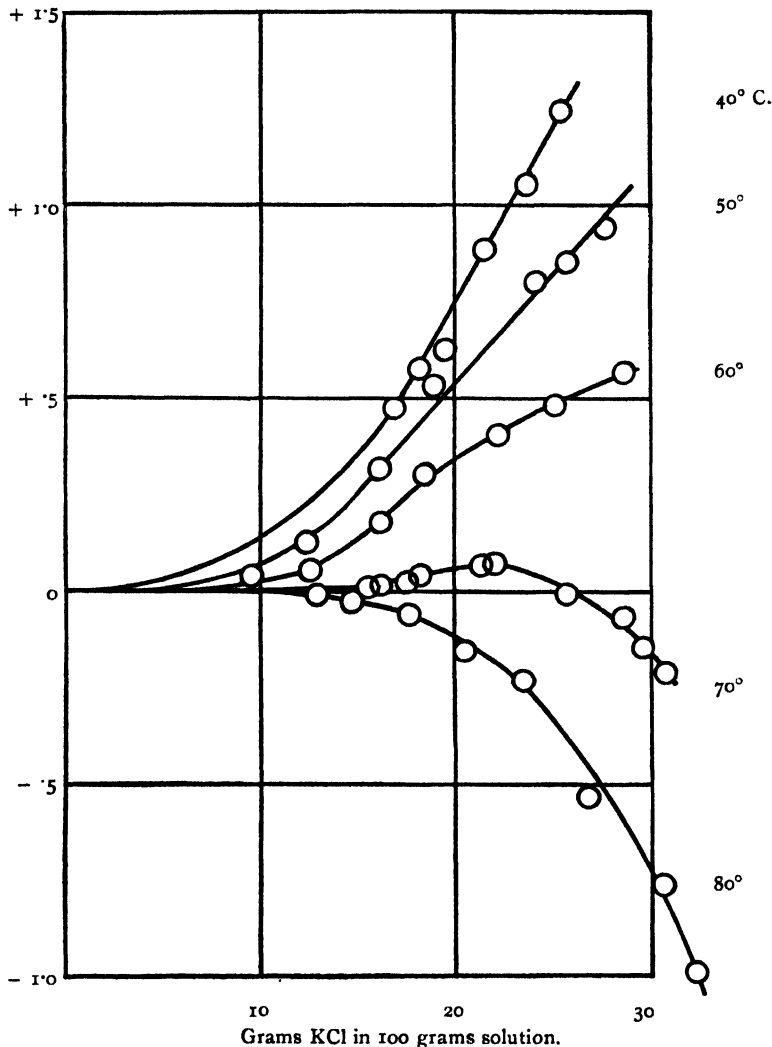


FIG. 4.

measurements were much more difficult. The results are shown graphically in Fig. 4; they indicate a change of sign at 70°C. At this temperature the

TABLE VI.—HEATS OF DILUTION OF POTASSIUM CHLORIDE SOLUTIONS.

Temperature.	C.	n/N.	N/n.	Heat.
40°00° C.	(Solid present)	—	—	+ 18°92
	27°26	0°09036	11°06	+ 1°51
	25°41	0°08256	12°12	+ 1°24
	23°86	0°07658	13°05	+ 1°05
	22°46	0°06984	14°32	+ 0°88
	19°54	0°03855	17°05	+ 0°62
	18°24	0°05379	18°60	+ 0°58
	17°00	0°04937	20°25	+ 0°47
50°00° C.	(Solid present)	—	—	+ 18°49
	27°86	0°09311	10°74	+ 1°18
	25°79	0°08377	11°93	+ 1°10
	19°03	0°05667	17°68	+ 0°53
	16°31	0°04700	21°28	+ 0°31
	12°33	0°03390	29°50	+ 0°12
	9°17	0°02434	41°08	+ 0°04
60°00° C.	(Solid present)	—	—	+ 18°28
	28°85	0°09777	10°22	+ 0°56
	25°26	0°08149	12°27	+ 0°47
	22°16	0°06865	14°57	+ 0°40
	18°53	0°05484	18°26	+ 0°30
	16°08	0°04619	21°65	+ 0°18
	12°64	0°03488	28°67	+ 0°06
70°00° C.	(Solid present)	—	—	+ 18°42
	30°87	0°1076	9°295	- 0°23
	29°67	0°1017	9°841	- 0°14
	28°86	0°09781	10°22	- 0°08
	25°71	0°09170	10°91	- 0°01
	22°97	0°07187	13°92	+ 0°03
	22°10	0°06841	14°62	+ 0°07
	21°43	0°06730	14°86	+ 0°06
	18°86	0°05605	17°84	+ 0°04
	18°28	0°05388	18°56	+ 0°02
	16°92	0°04910	20°37	+ 0°02
	16°29	0°04691	21°32	+ 0°01
80°00° C.	(Solid present)	—	—	+ 17°84
	32°28	0°1149	8°688	- 0°99
	30°57	0°1062	9°116	- 0°77
	26°77	0°08812	11°35	- 0°54
	23°60	0°07447	13°43	- 0°22
	20°32	0°06148	16°27	- 0°16
	17°66	0°05171	19°34	- 0°06
	14°87	0°04211	23°74	- 0°03
	12°7	0°03508	28°58	- 0°01

heat is positive up to about 26 per cent. KCl, and above that negative. The explanation of this change is not yet clear, but it is probably due to changes in hydration and ionisation. The relation of heat of dilution to temperature is also interesting (see Fig. 5). The lines are straight and intersect at about 70° C.

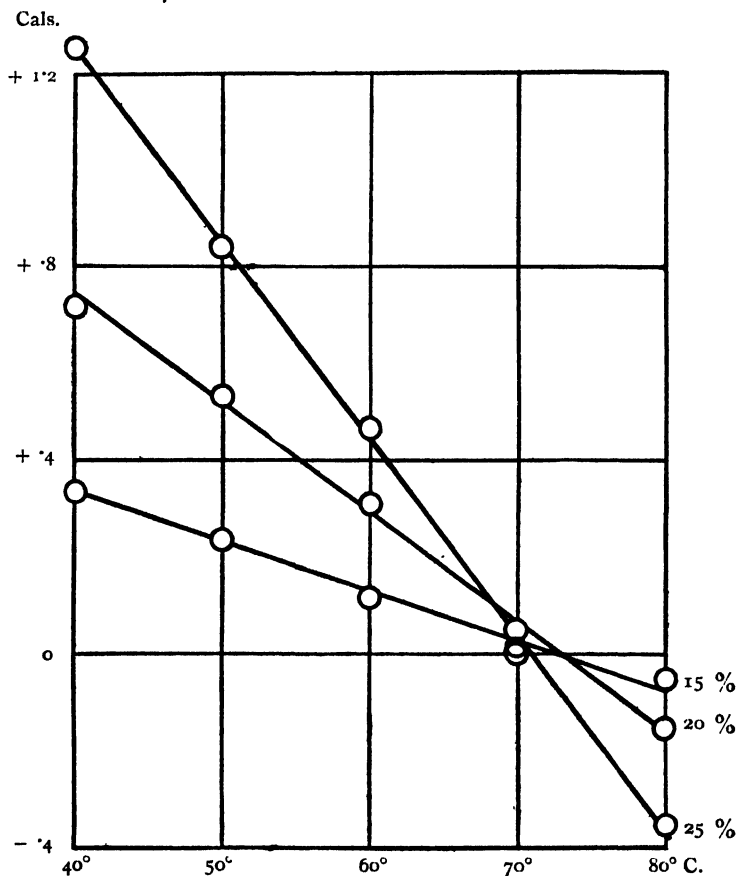


FIG. 5.

### Discussion of Results.

The general accuracy of the vapour pressure determinations has been estimated by comparing the observed value of the heat of dilution with those calculated from the vapour pressures by means of a more accurate form of the Kirchhoff equation put forward by Porter.<sup>1</sup>

The original equation

$$H = RT^2 \frac{\partial}{\partial T} \left( \log \frac{\pi_0}{\pi_\pi} \right) C$$

contained, amongst others, the assumption that the vapour of the solvent obeys the perfect gas law. Porter's improvement consisted in substituting, for the perfect gas law, Callendar's gas equation which holds extremely well

<sup>1</sup> *Trans. Far. Soc.*, 1917.

for water vapour. The effect of this substitution is to give an equation of the form:

$$H = T^2 \frac{\partial}{\partial T} \left( R \log \frac{\pi_0}{\pi_\pi} - \frac{c(\pi_0 - \pi_\pi)}{T} \right) C$$

$c$  is called the co-aggregation factor and is taken to vary with temperature; Callendar has given the values of  $c$  for water vapour at various temperatures.  $H$  is of course, the value for the differential heat of dilution of the solution whose concentration is given by  $C$ .

The values of  $H$  were calculated by plotting, on a large scale, values of the expression

$$R \log \frac{\pi_0}{\pi_\pi} - \frac{c(\pi_0 - \pi_\pi)}{T}$$

against temperature, for each concentration considered.

A smooth curve was drawn through the points obtained and then tangents were drawn in order to find the slope of the curve at various temperatures. The tangents were drawn by a variety of methods but the deviations from the mean value of the slope were only about 1 per cent.

The value of the correcting factor becomes smaller as  $\pi_\pi$  approaches  $\pi_0$  and is negligible when the solutions are dilute.

During the progress of the work, an attempt was made to find the relative change in  $H$  for a small error in  $\pi_\pi$  by differentiating the heat of dilution equation, but the resulting expression was incapable of even moderately simple treatment as a practical equation.

By calculating some trial cases, however, it has been shown that the results may be relied upon to approximately one-fifth of a mm.

The small value and rapid change in magnitude and, eventually, in sign of the heat of dilution of potassium chloride solutions, render it impossible to calculate accurate values for the heat from vapour pressures at only five temperatures. The most that can be done, is to plot against temperature, the values of the expression

$$R \log \frac{\pi_0}{\pi_\pi} - \frac{c(\pi_0 - \pi_\pi)}{T}$$

for various concentrations, and to show that the resulting curves represent approximately the facts as experimentally determined.

The curve for a 10 per cent. solution is simply a horizontal line. This line, which represents a negligible heat of dilution, is confirmed by direct determination.

For the more concentrated solutions, the curves indicate a small positive heat which becomes zero at about 70° C. and finally, at 80° C. negative; this also is confirmed by direct measurement.

In the derivation of Kirchhoff's equation, the assumption was made that the solute is involatile, which is true for both calcium and potassium chloride solutions.

In order to obtain an equation which included the heat of dilution, Trevor<sup>1</sup> suggested a form of the Gibbs-Helmholtz Equation.

$$PV = Q + T \cdot \frac{d(PV)}{dT}$$

$Q$  being positive when heat is evolved on dilution. This equation can only be integrated when  $Q$  is zero or does not vary with temperature. Supposing  $Q$  equals a constant  $A$ , we have on integration,

$$PV = RT + A$$

TABLE VII.—COMPARISON OF THE CALCULATED VALUES FOR THE HEAT OF DILUTION WITH THOSE DETERMINED EXPERIMENTALLY.

## CALCIUM CHLORIDE SOLUTIONS.

Concentration.	° C.	Calculated.	Observed.
10 per cent.	40	0·89	0·73
	50	0·95	0·76
	60	1·01	0·81
	70	1·08	1·03
	80	1·14	1·14
20 per cent.	40	2·5	2·8
	50	2·7	3·0
	60	3·0	3·1
	70	3·9	4·0
	80	4·3	4·6
30 per cent.	40	6·5	8·8
	50	7·4	9·4
	60	9·0	10·0
	70	11·8	12·1
	80	14·1	13·2
40 per cent.	40	27·4	30·2
	50	31·3	33·1
	60	36·6	36·0
	70	41·4	41·2
	80	44·9	47·1
50 per cent.	40	69·9	69·5
	50	74·5	75·5
	60	79·2	81·9
	70	84·0	84·0
	80	89·0	88·0

## POTASSIUM CHLORIDE SOLUTIONS.

10 per cent.	—	less than ·01 cal.	less than ·01 cal.
15 per cent.	40	+ 0·4	+ 0·35
	50	+ 0·3	+ 0·25
	60	0·0	+ 0·11
	70	— 0·1	0·0
	80	— 0·4	— 0·6
20 per cent.	40	+ 0·6	+ 0·72
	50	+ 0·5	+ 0·55
	60	+ 0·1	+ 0·32
	70	0·0	+ 0·04
	80	— 0·2	— 0·5
25 per cent.	40	+ 0·8	+ 1·25
	50	+ 0·6	+ 0·85
	60	+ 0·2	+ 0·49
	70	— 0·1	+ 0·02
	80	— 0·3	— 0·35

an expression which may be substituted in the van't Hoff equation,

$$PV = RT \frac{N}{n} \cdot \log \frac{\pi_0}{\pi_\pi}$$

giving 
$$RT + A = RT \cdot \frac{N}{n} \cdot \log \frac{\pi_0}{\pi_\pi}.$$

Bancroft<sup>1</sup> has shown that the taking into account of the heat of dilution, as is done in this equation, is sufficient to remove many anomalies from molecular weight determinations, for which cumbrous and doubtful hypotheses had been devised. Thus sodium, in mercury, has an apparent molecular weight of 16, an impossible figure, raised to nearly 23 when account is taken of the heat of dilution; a similar simplification was observed in the case of sulphuric acid.

The heat of dilution of solutions of calcium and potassium chloride changes rapidly with temperature, as may be seen from the curves submitted. Nevertheless, as merely an approximation, the above equation was applied to the case of a 30 per cent. calcium chloride solution at 40° C. The value of the molecular weight was given as 54, compared with 20 when no account was taken of the heat of dilution; 54 as against 111 (the theoretical mol. wt.) is not unreasonable, because it can be explained by postulating ionisation of the calcium chloride to the extent of about 50 per cent. A value of 20 would require a special hypothesis such as "removal" of the water from the solution due to hydrate formation.

The above equation was applied to urea, data for the vapour pressure and the heat of dilution for solutions of which are given by Perman and Lovett.<sup>2</sup> In the case of a 30 per cent. solution, for which the heat of dilution is fairly constant with temperature, a true molecular weight of 59 is given instead of an apparent value of 67 (theoret. 60) obtained by neglecting the heat of dilution.

For a 60 per cent. solution, for which the heat of dilution showed a far greater change with temperature, the corrected value was 57.

### Summary.

### PARTS II. AND III.

(1) The statical method of measuring vapour pressures of solutions devised by Perman and Saunders<sup>3</sup> has been improved in various respects.

(2) Using this method, the vapour pressures of aqueous solutions of potassium chloride, and calcium chloride whose concentration ranged from zero to saturation, have been measured at five temperatures, *viz.* :

40.00° C., 50.00° C., 60.00° C., 70.00° C., 80.00° C.

(3) The densities of these solutions have been determined over the same range of temperature and concentration.

(4) An original method has been devised whereby the heats of dilution of substances may be determined electrically. This method is independent of the sign of the heat change and may be employed over a range of temperature.

(5) The heat of dilution of the above solutions has been determined over the same temperature range as the vapour pressures.

<sup>1</sup> *J. Physical Chem.*, 1906.

<sup>2</sup> *Trans. Far. Soc.*, 1926.

<sup>3</sup> *Ibid.*, 19, Pt. II.

(6) The differential heat of dilution as defined by Kirchhoff's equation (the relation between heat of dilution and concentration) and the variation of heat of dilution with temperature have been determined from the results obtained.

(7) Calcium chloride has a large negative heat of dilution which increases with temperature.

(8) The heats of dilution of calcium chloride solutions calculated from the vapour pressures, agree in sign and order with those determined directly.

(9) Potassium chloride has a very small positive heat of dilution at  $40^{\circ}\text{C.}$ , the lowest temperature for which it was determined. The heat changes sign at about  $70^{\circ}\text{C.}$ , becoming positive for all concentrations at  $60^{\circ}\text{C.}$

(10) The initial and final signs, temperature of transition, and the order of the heat of dilution as determined directly, are confirmed by the various values calculated from the vapour pressure data for the potassium chloride solutions.

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# CONDITION OF SILVER CHROMATE IN GELATINE FROM ELECTRIC CONDUCTIVITY AND DIFFUSION EXPERIMENTS.

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In foregoing papers,<sup>1</sup> it has been shown that the concentration of silver nitrate necessary to turn a yellow sol of silver chromate in gelatine red, goes on increasing as the concentration of the yellow sol decreases. Moreover, the solubility product of silver chromate goes on increasing as the concentration of the gelatine gel increases and this product, instead of keeping constant for the same concentration of gelatine, goes on decreasing as the concentration of the yellow sol of silver chromate is increased. If the peptisation of silver chromate in gelatine followed the ordinary rules of solubility product, as has been assumed by Williams and Mackenzie,<sup>2</sup> this product should have been constant, but it is not so. Hence we have concluded that the ordinary solubility relations do not apply to these cases of peptisation.

Moreover, we have shown that the yellow sol of silver chromate is negatively charged owing to the preferential adsorption of chromate ions and, when the yellow sol is changed to red by the addition of silver nitrate, the change of colour is accompanied by a reversal of the charge. The red sol of silver chromate is positively charged due to the adsorption of silver ions. We are of the opinion that the red sol is more unstable than the yellow one.

We have found out that the amount of silver chromate (solubility product) that can remain in suspension in 5.67 per cent. gelatine has the value  $3.38 \times 10^{-7}$ . Comparing this value with the solubility product of silver chromate in water at 29° ( $4.2 \times 10^{-12}$ ), we get the ratio  $8.04 \times 10^4$ . Hence our experimental results show that large quantities of silver chromate can exist in the peptised condition in gelatine.

Further evidence in favour of the existence of silver chromate in the colloidal state is brought forward in this paper by measuring its electric conductivity in gelatine.

Experiments were undertaken to find out the conductivity of silver chromate of different concentrations in 3 per cent. gelatine at 35°. As silver chromate was produced by the addition of equivalent quantities of silver nitrate and potassium chromate to the gelatine, an equivalent amount of potassium nitrate was simultaneously produced. In order to ascertain the conductivity of silver chromate alone, the conductivity of an equivalent concentration of potassium nitrate alone in gelatine was determined under identical conditions.

A typical result of conductivity experiments is shown in Table I.

Exactly similar results were obtained with other concentrations of the electrolytes and the results obtained are summarised in Table II.

From the conductivity measurements given in Table I., the conductivity of silver chromate as determined by experiments can be ascertained by simply subtracting the conductivity of potassium nitrate from

that of the mixture of potassium chromate and silver nitrate. If it is supposed that silver chromate remains in the ionic condition and not in the colloidal state, then its conductivity should be equal to the sum of the conductivities of potassium chromate and silver nitrate *less* the conductivity of potassium nitrate. Table II. contains the results calculated on the basis of the above considerations from the observations on electric conductivity.

TABLE I.

Concentrations of silver chromate, potassium nitrate, potassium chromate and silver nitrate used . . .	N/520.
Conductivity of water at 35° . . . . .	$8.904 \times 10^{-6}$ mhos.
Conductivity of gelatine at 35° . . . . .	$1.1868 \times 10^{-3}$ "
Conductivity of gelatine and potassium chromate at 35° . . . . .	$1.4362 \times 10^{-3}$ "
Conductivity of gelatine and silver nitrate at 35° . . . . .	$1.4187 \times 10^{-3}$ "
Conductivity of gelatine, silver nitrate and potassium chromate at 35° . . . . .	$1.4451 \times 10^{-3}$ "
Conductivity of potassium nitrate in gelatine at 35° . . . . .	$1.4041 \times 10^{-3}$ "

TABLE II.

Concentration of Silver Chromate.	Conductivity Observed.	Conductivity as Calculated from the Experiments, assuming $\text{Ag}_2\text{CrO}_4$ to be in the Ionic Condition.
N/520 . . . . .	$0.0410 \times 10^{-3}$ mhos.	$0.2640 \times 10^{-3}$ mhos.
N/186.7 . . . . .	$0.154 \times 10^{-3}$ "	$0.4092 \times 10^{-3}$ "
N/145 . . . . .	$0.073 \times 10^{-3}$ "	$0.4884 \times 10^{-3}$ "
N/120 . . . . .	$-0.0831 \times 10^{-3}$ "	$0.4579 \times 10^{-3}$ "

In all these experiments, "Nelson's A2" gelatine was used.

From the above table it will be seen that, if silver chromate were present in the ionic condition as was supposed by Williams and Mackenzie,<sup>3</sup> the conductivity of this substance would have been much greater than the values actually obtained. In the last case, the minus sign indicates that the conductivity of a mixture of silver chromate and potassium nitrate is less than the conductivity of potassium nitrate alone. As the amount of silver chromate present in the last set is sufficiently large, it seems that silver chromate in the course of its formation has probably adsorbed some potassium nitrate, thereby lowering its active concentration.

Moreover, silver chromate sol prepared by the addition of equivalent quantities of silver nitrate and potassium chromate to gelatine solution shows Brownian movement when seen through an ultra-microscope, proving thereby the truly colloidal nature of the substance.

Though the evidence given above forces us to conclude that silver chromate in gelatine exists in the colloidal state, yet to test the conclusion of Williams and Mackenzie that "the silver chromate does not behave as a protected colloid but as a crystalloid," experiments on diffusion were again undertaken.<sup>3</sup> In order to find out whether silver chromate produced by the addition of equivalent quantities of silver nitrate and potassium chromate to a gelatine solution can diffuse into water placed on the top, the following experiments were undertaken:—

A number of test tubes each containing 10 c.c. of 3 per cent. gelatine were taken and to each of them different amounts of equivalent quantities of N/20 silver nitrate and N/20 potassium chromate were added. When the silver chromate-gelatine gel had set in the above test tubes,

2 c.c. of pure 3 per cent. gelatine were poured gradually over the mixture and then 10 c.c. of distilled water were placed at the top of the pure gel after it had set. The diffusion was allowed to continue for about a week in each case. The quantity of silver chromate was gradually increased from  $1.415 \times 10^{-3}N$  (at which the colour of silver chromate was yellow) to  $1.1 \times 10^{-2}$  when the colour of silver chromate became red. In the following table the results are given :—

TABLE III.

No.	Concentration of Silver Chromate in the Lower Gel.	Colour of the Lower Gel.	The Colour of Water Placed at the Top.	Remarks.
1	$1.415 \times 10^{-3}N$	Yellow.	Yellowish.	On the addition of silver nitrate to the supernatant liquid only a red colour was produced but it gave no precipitate with HCl, indicating the absence of silver ions.
2	$2.741 \times 10^{-3}N$	Do.	Yellow.	Silver nitrate produced a red precipitate when added to the upper liquid, but HCl did not give a precipitate with it
3	$3.070 \times 10^{-3}N$	Do.	Do.	Do. do.
4	$4.60 \times 10^{-3}N$	Reddish.	Deep yellow.	Do. do.
5	$5.903 \times 10^{-3}N$	Red.	Do.	H <sub>2</sub> S water produced no black coloration and HCl gave no white precipitate when added to the supernatant liquid, while on the addition of silver nitrate a red precipitate was produced.
6	$6.618 \times 10^{-3}N$	Do.	Do.	Do. do.
7	$7.715 \times 10^{-3}N$	Do.	Do.	Do. do.
8	$8.33 \times 10^{-3}N$	Do.	Do.	Do. do.
9	$9.376 \times 10^{-3}N$	Do.	Do.	Do. do.
10	$1.10 \times 10^{-2}N$	Do.	Do.	Do. do.

In all the above test tubes the supernatant liquid was coloured yellow, but in none of them could any trace of silver ions be detected by adding either H<sub>2</sub>S water or hydrochloric acid, while distinct precipitate of chromates was obtained when either silver nitrate or lead acetate was added to the supernatant liquid, showing conclusively the presence of chromate ions.

We have also been able to obtain results similar to those of Williams and Mackenzie in the production of rings of silver chromate by diffusing either silver nitrate or potassium chromate into gelatine gel containing equivalent quantities of silver nitrate and potassium chromate.

Experiments similar to those described above were undertaken with this difference only that instead of 10 c.c. of water, 2 c.c. of different concentrations of either silver nitrate or potassium chromate were allowed to diffuse from the top of the pure gel. In these experiments 5 per cent. gelatine was used instead of 3 per cent. as in the previous case and different amounts of equivalent quantities of silver nitrate and

## 26      CONDITION OF SILVER CHROMATE IN GELATINE

potassium chromate were added to it. Only such concentrations of silver chromate were used as gave a yellow colour to the lower gel.

The following results were obtained by diffusing silver nitrate from the top after four days :—

TABLE IV.

No.	Concentration of Silver Chromate in the Lower Gelatine Gel.	Concentration of Silver Nitrate Diffusing from the Top.	Remarks.
1	$5.46 \times 10^{-3}N$	$1.00 N$	No rings ; but the lower gel turned red and gave a continuous precipitate.
2	$5.46 \times 10^{-3}N$	$5.0 \times 10^{-1}N$	Do. do.
3	$4.10 \times 10^{-3}N$	$1.00 N$	Do. do.
4	$4.10 \times 10^{-3}N$	$5.0 \times 10^{-1}N$	Do. do.
5	$3.447 \times 10^{-3}N$	$1.00 N$	The yellow colour of the lower gel turned red. There was a precipitate in which rings were visible.
6	$3.447 \times 10^{-3}N$	$5.0 \times 10^{-1}N$	Do. do.
7	$2.0 \times 10^{-3}N$	$1.00 N$	Do. do.
8	$2.0 \times 10^{-3}N$	$5.0 \times 10^{-1}N$	Do. do.
9	$1.8 \times 10^{-3}N$	$1.00 N$	Do. do.
10	$1.8 \times 10^{-3}N$	$5.0 \times 10^{-1}N$	Do. do.
11	$5.0 \times 10^{-4}N$	$1.00 N$	The lower gel produced a very thin red continuous deposit.
12	$5.0 \times 10^{-4}N$	$5.0 \times 10^{-1}N$	Do. do.

From the foregoing table it will be seen that, in order to produce rings, the concentration of the sparingly soluble salt should be within a definite limit. If its strength either exceeds or falls short of this particular limit, then in neither case does ring production take place. This will be discussed later, in detail.

Experiments similar to those described above were undertaken to find out if there is any relation existing between the concentration of the diffusing electrolyte and that of the sparingly soluble salt, when ring formation takes place.

Hence different strengths of silver nitrate solution were allowed to diffuse into a number of test tubes containing the same concentration of silver chromate uniformly distributed in the lower gel. The results are set out in Table V.

That the change from yellow to red in the colour of silver chromate present in the lower gel is due only to the influence of silver ions is further proved by the fact that any soluble salt of silver other than nitrate, e.g. silver sulphate, also gives exactly similar results. Instead of diffusing silver nitrate from the top a fairly concentrated solution of silver sulphate was diffused into a number of tubes containing  $3.447 \times 10^{-3}N$  silver chromate; in Table VI. the results were obtained after diffusion had proceeded for four days.

TABLE V.

No.	Concentration of Silver Chromate in the Lower Gelatine Gel.	Concentration of Silver Nitrate Diffusing from the Top into the Gel.	Remarks.
1	$3.447 \times 10^{-3}N$	$1.00N$	The yellow colour of the lower gel turned red. There was a precipitate in which rings were visible.
2	Do.	$5.0 \times 10^{-1}N$	Do. do.
3	Do.	$2.5 \times 10^{-1}N$	Do. do.
4	Do.	$1.25 \times 10^{-1}N$	Do. do.
5	Do.	$6.25 \times 10^{-2}N$	The lower gel turned red, but the precipitate was more or less continuous with very faint traces of ring formation.
6	Do.	$3.125 \times 10^{-2}N$	Do. do.
7	Do.	$5.0 \times 10^{-2}N$	Do. do.
8	Do.	$2.5 \times 10^{-2}N$	Lower gel turned red; gave continuous deposit
9	Do.	$1.25 \times 10^{-2}N$	Do. do.
10	Do.	$0.625 \times 10^{-2}N$	Do. do.

TABLE VI.

No.	Concentration of Silver Chromate in the Lower Gelatine Gel.	The Electrolyte Diffused from the Top.	Remarks.
1	$3.447 \times 10^{-3}N$	Silver sulphate.	A red precipitate appeared in the lower gel, which when seen in transmitted light gave the appearance of broad rings.
2	Do.	Do.	Do. do.
3	Do.	Do.	Do. do.
4	Do.	Do.	Do. do.

More or less similar results have been obtained by Williams and MacKenzie by the diffusion of different concentrations of silver nitrate into gelatine containing a yellow sol of silver chromate.

Exactly similar experiments were undertaken to find out the effect of diffusing potassium chromate into gelatine gel containing silver chromate uniformly distributed in it. Gelatine containing different strengths of silver chromate was allowed to set in test tubes. After it had set, 2 c.c. of 5 per cent. gelatine were poured on the top and, after this had set, 2 c.c. of different strengths of potassium chromate were diffused from the top. The concentration of silver chromate in the lower gel was always less than  $6.4 \times 10^{-3}N$ , which is the limiting concentration in 3.43 per cent. gelatine at  $30^{\circ}C$ . beyond which silver chromate turns red

## 28 CONDITION OF SILVER CHROMATE IN GELATINE

and, consequently, the colour of the lower gel in every test tube was yellow.

The following results were obtained after allowing potassium chromate to diffuse from the top into the gel for about a week :—

TABLE VII.

No	Concentration of Silver Chromate in the Lower Gelatine Gel.	Concentration of Potassium Chromate Diffused from the Top into the Gel.	Remarks.
1	$3.447 \times 10^{-3}N$	$1.00N$	No change observed.
2	$4.16 \times 10^{-3}N$	$1.00N$	A reddish tinge appeared in the lower yellow gel but no precipitate.
3	$3.447 \times 10^{-3}N$	$5.0 \times 10^{-1}N$	No change.
4	Do.	$2.5 \times 10^{-1}N$	Do.
5	Do.	$5.0 \times 10^{-2}N$	Do.
6	Do.	$2.5 \times 10^{-2}N$	Do.
7	Do.	$1.25 \times 10^{-2}N$	Do.
8	Do.	$0.625 \times 10^{-2}N$	Do.
9	Do.	$1.0 \times 10^{-1}N$	Do.
10	$4.508 \times 10^{-3}N$	$1.0 \times 10^{-1}N$	A precipitate appeared in the lower yellow gel, but, however, no rings could be observed.
11	$4.840 \times 10^{-3}N$	$5.0 \times 10^{-2}N$	Do. do.

From the above table it can be seen that potassium chromate can coagulate and change a yellow sol of silver chromate into a red one when the concentration of silver chromate is near the maximum limit at which it can remain yellow in the peptised condition. On the other hand, if the concentration of silver chromate be much less than the above limiting value it is difficult even for fairly concentrated potassium chromate solutions to produce any precipitation, as can be seen from the fact that  $3.447 \times 10^{-3}N$  silver chromate is *not* changed by diffusing various concentrations of potassium chromate into it.

But if the concentration of silver chromate is increased potassium chromate, of such concentrations that at first it fails to produce a change, can bring about coagulation and thus give rise to precipitation.

Exactly similar results have been obtained by Williams and Mackenzie.<sup>4</sup> Table VIII. has been calculated from their data: Limiting concentration at which silver chromate can remain in suspension,  $4.3 \times 10^{-3}N$  in 3 per cent. gelatine.

From the above table of Williams and Mackenzie's results, it can be seen that potassium chromate produces a precipitate in the lower gel in all cases. This is due to the fact that the concentration of silver chromate used is very near the limiting value,  $4.3 \times 10^{-3}N$ , and it is due to this nearness to the limiting value that potassium chromate in all the concentrations used could bring about a change.

It should be emphasised that the yellow colour of the top layer of

gelatine, observed by Williams and Mackenzie in their experiments on diffusion, is certainly due to the existence of free potassium chromate and not silver chromate as has been assumed by the above authors. We have repeatedly observed that though the upper layer of gelatine or of pure water becomes yellow when the diffusion experiments are over, the presence of silver ions or of silver chromate cannot be detected. Hence the yellow colour of the top gel or water is due to the diffusion of the free potassium chromate from the lower jelly.

TABLE VIII.

No.	Concentration of Silver Chromate in the Lower 3 per cent. Gelatine Gel.	Concentration of Potassium Chromate Diffusing from the Top.	Remarks.
1	$4.166 \times 10^{-3}N$	$5.0 \times 10^{-1}N$	General precipitation with banded structure visible.
2	Do.	$1.0 \times 10^{-1}N$	Thick bands.
3	Do.	$2.0 \times 10^{-1}N$	Do.
4	Do.	$1.0 \times 10^{-2}N$	Do.
5	Do.	$5.0 \times 10^{-3}N$	Haze.
6	Do.	$4.0 \times 10^{-3}N$	Do.

We have made the above observations on the peptisation of silver chromate in presence of gelatine. We have also proved by diffusion experiments that in all cases where the lower layer of gel consisted of pure silver chromate obtained by the addition of silver nitrate and an equivalent amount of potassium chromate, and the superimposed layer was either distilled water or pure gelatine, the upper gel or water always contained traces of potassium chromate after diffusion; this can be tested by silver nitrate or lead acetate. It appears, therefore, that when equivalent amount of silver nitrate is added to the gel containing a definite amount of potassium chromate the reaction is either never completed or a small amount of silver nitrate is used up in some other way. From his researches, Paul<sup>5</sup> has assumed that gelatine forms compounds with electrolytes. Similar views have also been expressed by Robertson<sup>6</sup> in his experiments on the precipitation of casein by salts of heavy metals. We are of opinion that gelatine can adsorb silver ions, more readily and in greater quantities than chromate ions, from equally concentrated solutions of silver nitrate and potassium chromate. Consequently, when equivalent quantities of silver nitrate and potassium chromate are mixed in presence of gelatine or any other albuminous matter, there is always an excess of chromate ions, because of the preferential adsorption of silver ions by the albuminous matter.

Bolam and Mackenzie<sup>7</sup> have determined the electric conductivity of silver chromate in gelatine and have found that the observed conductivity is appreciably less than the conductivity calculated on the basis that the silver chromate exists wholly as ions in gelatine. They have tried to determine the silver ion concentration from silver chromate in gelatine. The results, however, seem to be somewhat inconclusive. Thus, they observed that the *E.M.F.* changes when the cell is left in the

thermostat. Moreover, they obtained practically the same silver ion concentration, when the concentration of silver chromate was  $333 \times 10^{-5}N$  or  $236 \times 10^{-5}N$  or  $162 \times 10^{-5}N$ . In other words, their results show that the concentration of silver ions is the same even if the concentration of silver chromate is halved. They conclude: "The foregoing makes it appear probable that in the silver chromate gelatine mixtures, that part of the silver and chromate which was not present as ions was combined in some fashion with the gelatine."

It appears to us that the hydrogen ions present in gelatine have reacted on silver chromate with the formation of silver ions and chromic acid (e.g.  $\text{Ag}_2\text{CrO}_4 + 2\text{H}^+ \rightleftharpoons 2\text{Ag}^+ + \text{H}_2\text{CrO}_4$ ). Consequently in presence of gelatine containing  $\text{H}^+$ , the concentrations of  $\text{Ag}^+$  ions and of chromic acid appear greater than those available from a saturated solution of  $\text{Ag}_2\text{CrO}_4$  in water.

The recent experiments of Bolam and Mackenzie showing that the chromate appeared to be the more free of the two ions, e.g. silver and chromate,<sup>8</sup> are in support of the conclusion of Sen and Dhar that chromate ions are obtained in the upper layer by diffusion and not silver chromate as was assumed by Williams and Mackenzie. The diffusion experiments described in this paper confirm the conclusion of Sen and Dhar.

### Summary and Conclusion.

(1) Measurements of electric conductivity of silver chromate of varying concentrations in gelatine show that the observed conductivity is much less than the conductivity calculated on the assumption that silver chromate exists wholly as ions in gelatine.

(2) Diffusion experiments show that chromate ions (and not silver chromate) diffuse in gelatine placed on the top of a gel containing silver nitrate and an equivalent quantity of potassium chromate.

(3) The chemical change between silver nitrate and an equivalent quantity of potassium chromate is not complete in presence of gelatine, an amount of potassium chromate remains free. An explanation of this behaviour, based on the more marked adsorption of silver ions than that of chromate ions by gelatine, has been advanced.

(4) When silver salts are allowed to diffuse in gelatine gel containing silver chromate, rings are formed only when the concentration of silver chromate is within a definite limit.

(5) Potassium chromate can coagulate and change a yellow sol of silver chromate into a red one when the concentration of silver chromate is nearer the limit at which it can remain yellow in the peptised condition.

(6) Experimental results on electric conductivity, on diffusion or on coagulation prove that silver chromate exists in pure gelatine mainly in the colloidal condition and that Liesegang rings are produced by the coagulation of this peptised substance.

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- <sup>2</sup> *J.C.S.* (1920), **117**, 844.
- <sup>3</sup> Compare Sen and Dhar, *Kolloid Z.* (1924), **34**, 270.
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# THE ACTINIC ABSORPTION OF CHLORINE GAS, WITH RESPECT TO THE HYDROGEN CHLORINE REACTION.

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## I. Introduction.

In dealing with the phenomena of photo-chemical reactions and molecular activation by the action of light, a method of investigation which has attracted comparatively little attention is that of subjecting the illuminating radiation to various perturbing influences and observing the resulting change in the reaction initiated. Progress has been made chiefly in the study of the results of changing the frequency and the intensity. The latter has unfortunately been the subject of much diversity of opinion and the former is bound up with it, inasmuch as experimental work has not yet been carried out with monochromatic light of which the frequency but not the intensity has been varied.

It should however be possible to pursue investigations in a different way by using an intense beam of white light and a filter in which the activated substance itself is the filtering medium. Although we are thus using the integrated effects from a whole wave-band, yet the composition of the emergent light may be varied in a known manner by altering the absorption spectrum; an analysis of the results might possibly bring fresh evidence to bear upon the problem of molecular activation.

The first experiment which suggests itself is to alter the composition of the light simply by increasing the effective thickness of the absorbing medium. For convenience we may employ the old terms "actinic power" and "actinic extinction" for the sake of their descriptive values. If now a beam of white light be passed through a filter tube containing chlorine gas at a given pressure and, then, allowed to fall upon a reaction vessel so as to induce the photo-chemical union of hydrogen and chlorine, the velocity of that reaction may be taken as a measure of the actinic power of the beam. It is also a measure of the actinic absorption which has been carried out by the gas in the filter tube. By varying the pressure in the filter, and hence the concentration of the absorbing medium, and observing the corresponding changes in the reaction velocity, the actinic extinction curve is obtained. Bunsen and Roscoe gave this idea in 1857, but it would seem that an extension of their work is greatly to be desired in view of the problems now confronting photo-chemistry.

The determination of the actinic extinction coefficient has been attempted before, but the literature is again contradictory. Bunsen and

Roscoe in their classical researches included the measurement of this quantity<sup>1</sup> and found that when a coal gas flame was used as the illuminant, a column of chlorine 17.17 cm. long reduced the actinic power of the light to 10 per cent. They also varied the partial pressure of the chlorine by diluting it with air, but it must be noted that only four separate readings were taken in the latter case and two when the length of the filter tube was altered.

In strange contradiction to this, Mellor<sup>2</sup> in 1902 found that a depth of chlorine of 10 to 15 cms. completely removed the actinic power from the light. He said, "When a bulb of hydrogen and chlorine gas is placed in a sufficiently large jar of moist chlorine gas and exposed to light, the bulb is perfectly screened from the actinic rays for an indefinite period." Much, however, would depend upon the intensity of illumination employed.

## 2. Experimental Work.

The rate of the combination of hydrogen and chlorine under the influence of light may be determined by several methods, but the actinometer arrangement of Bunsen and Roscoe, subsequently used by Burgess and Chapman<sup>3</sup> was considered to be the most suitable since it enables the whole course of the reaction to be followed. In principle, the actinometer consists of a bulb containing a mixture of hydrogen and chlorine together with a little water to absorb the HCl formed by the reaction. This bulb is connected with a narrow bore index tube so that the contraction of the gas volume may be followed by the movement of an indicator. Side tubes with stop-cocks serve to admit and extract gas at will. In order to obtain the pattern which should combine the best proportions for size of bulb and diameter of index tube, eight different actinometers were constructed and compared in efficiency. It seemed to be of little advantage to increase the size of the bulb beyond certain limits; the final readings were made with one of 7 cm. diameter and spherical form. The apparatus was repeatedly cleansed internally with a mixture of chromic and nitric acids and, finally, a little distilled water was introduced to lie at the bottom of the bulb.

The gas mixture was prepared by electrolysis from pure concentrated hydrochloric acid. The chief drawback is the evolution of oxygen at the anode as the concentration of the acid falls;<sup>4</sup> to overcome this, some workers<sup>5</sup> have used large quantities of acid; in the present experiments, a glass chamber holding  $2\frac{1}{2}$  litres was employed. The electrodes together with two glass tubes passed through a stopper, sealed in and protected from the action of chlorine by "pizein" wax. Before commencing operations, a stream of chlorine gas was passed through the whole system for several hours in order to sweep out all traces of air and to saturate all the liquids. The electrolysis was then commenced and the mixed gases were allowed to pass for several more hours, the bulb of the actinometer being strongly illuminated by an arc light meanwhile. The anti-catalysts were thus attacked by the activated chlorine and, in time, were removed from the system.

The reaction system was immersed in a large thermostat-bath consisting of a tank of 20 gallons capacity fitted with a plate-glass port-hole in one

<sup>1</sup> Bunsen and Roscoe, *Phil. Trans.*, 1857, 147, 601.

<sup>2</sup> Mellor, *J.C.S.*, 1902, 81, 1280.

<sup>3</sup> Burgess and Chapman, *J.C.S.*, 1906, 89, 1399.

<sup>4</sup> Chapman and MacMahon, *J.C.S.*, 1909, 95, 135.

<sup>5</sup> Coehn and Jung, *Z. physikal. Chem.*, 1924, 110, 720.

side through which light could be passed. The bulb was only a centimetre from the port-hole so that the light absorbed by the water was negligible.

The illumination was provided by a "white" beam from a Pointolite lamp. After being rendered parallel by a lens, the light passed first through a shutter, then through the filter tube and, lastly, through the port-hole in the tank. The filter consisted of a glass tube of 5 cms. diameter, and 45 cm. length, fitted with two glass side-tubes for gas manipulation. The ends were closed with plane pieces of glass, sealed on with "pizein" and the whole was capable of holding a good vacuum. The filter tube was in connection with a pump, a gas supply tube and a manometer in which mercury covered with a long column of paraffin was used. In spite of the paraffin layer, the action of the chlorine on the mercury necessitated a re-cleaning operation every day, the deposits of mercury chlorides being removed with aqua regia.

It is notorious that previous quantitative work with an actinometer of this type has been productive of the most directly conflicting results, particularly in the investigation of a problem very analogous to the present one, namely the influence of light intensity on the reaction.<sup>1</sup> Since it was possible, therefore, that some serious source of error might be inherent in the method, the experimental procedure was developed very carefully and a study was made of the degree of accuracy with which results could be repeated.

For any one exposure to white light, a satisfactory curve could always be obtained on plotting the index reading with time. The Draper expansion was followed by a steady reaction velocity, the points lying very well on a straight line which could be prolonged for the whole length of the index tube (about 4 feet) without sensible deviation. When however the reaction velocity thus obtained was compared with another value obtained under precisely the same external conditions, it became evident that enormous variations were possible. The velocity was altered whenever fresh bubbles of gas were admitted to the actinometer, or when the reaction was interrupted, *i.e.* when the light was cut off and a dark period interposed between the two parts of an exposure. Over 200 exposures were made to examine this phenomenon, and it was found that the reactivity of the mixture was reduced by (1) admission of new gas, (2) an effect bequeathed from the preceding exposure, which developed during the following dark period. These results were in accordance with the theories of inhibiting agents advanced by previous workers, as may be shown briefly. The reaction velocity may be regarded as the product of three terms, the light intensity, the frequency of the radiation, and a quantity which we may call the "sensitivity factor" *S*, depending upon the quantity of anti-catalyst present. Any agency which will alter the concentration of anti-catalyst present will also modify the value of *S*. We are of course dealing here with an anti-catalyst belonging to the first class of inhibitors as distinguished by Norrish,<sup>2</sup> since the reaction is merely diminished in velocity and not totally arrested. Now it is known that oxygen is an anti-catalyst of this type, and this affords an explanation of the observed results, since oxygen may be admitted in two ways: (1) with fresh gas from the generator, due to anodic liberation, and (2) during an exposure, when the light falling on the water in the bulb liberates oxygen as the result of a photo-chemical action between the water and the dissolved chlorine. It may be added that the illuminated

<sup>1</sup> Briers, Chapman and Walters, *J.C.S.*, 1926, 129, 562; also Baly and Barker, *J.C.S.*, 1921, 119, 653.

<sup>2</sup> Norrish, *J.C.S.*, 1925, 127, 2323.

chlorine has itself the power of removing the free oxygen by the Weigerts reaction.<sup>1</sup>

These sources of error having been revealed, it was obvious that readings under different external conditions were only to be trusted when it was certain that the factor  $S$  was constant. Since this would have involved great experimental difficulties, a method was devised whereby the effect of a variation in  $S$  was taken into account. It was based on the observed fact that during the duration of any single uninterrupted exposure, the reaction velocity  $V$  and, hence,  $S$  also remained constant, presumably owing to the fact that there was a short time lag in the photo-chemical evolution of oxygen from the water. A second source of white illumination, "B," was provided and used as a standard. The procedure was then to commence an exposure with "B," exchange for the illumination under examination by the operation

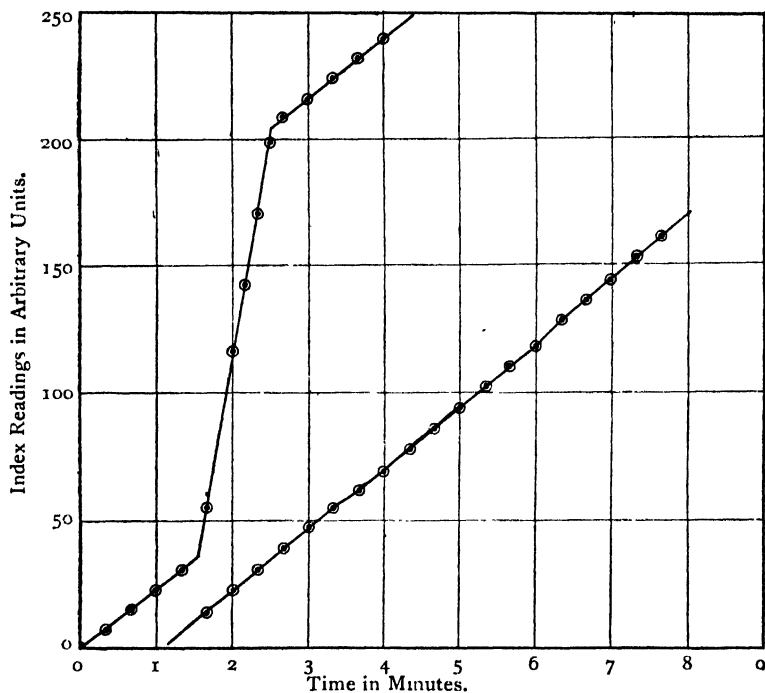


FIG. 1.—Types of reaction velocity curves obtained.

of a switch and, finally, to exchange for "B" again. A curve with two discontinuities was then obtained, the first and last portions of which were found to have the same gradient. The gradient of the middle portion was then calculated relatively to this common standard. This corrected reaction velocity was independent, within limits, of the sensitivity factor  $S$  and, in practice, only those values were used which entailed a correction of less than 10 per cent. Specimen curves are shown in Fig. 1.

In operating the filter tube, the procedure was as follows: An exposure having been given for white light, the filter tube was pumped out and the chlorine was permitted to flow through under pressure from a cylinder for a minute or two. The chlorine was then cut off and the pressure was reduced to a selected value at which it was left while an exposure was given to the

<sup>1</sup> Norrish and Rideal, *J.C.S.*, 1925, 127, 787.

actinometer. The pressure in the filter was read off on the manometer and tabulated along with the corresponding value of the reaction velocity calculated as described from the time-index curves. A complete series of readings was always taken without interruption and occupied about 12 hours when all precautions were included. The gas pressures were not taken in ascending order, but were alternated at random. Several complete sets of readings were obtained, one of which is shown in Fig. 2, the values

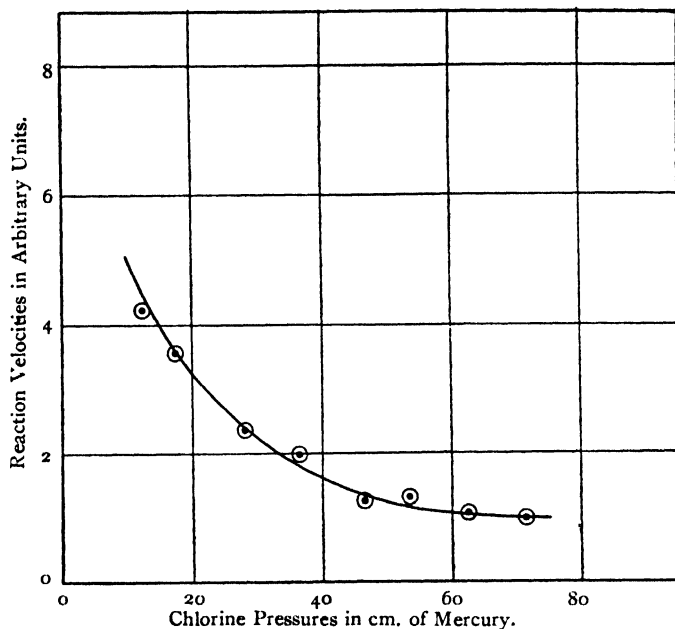


FIG. 2.

being tabulated below:—

TABLE I.

Temperature of Gas 18° C.	Tube 45 Cms. Long		
Pressure of Chlorine in Filter Tube (in Cms. of Hg).	Mean Value of Reaction Velocity with Standard Light	Value of Reaction Velocity with Light through Filter.	Relative Reaction Velocity.
32.0	1.32	4.60	3.56
46.4	1.72	2.12	1.23
62.4	1.70	1.80	1.06
17.4	1.51	5.32	3.53
53.4	1.30	1.85	1.42
28.0	1.16	1.14	0.99
36.4	0.96	1.90	1.98
12.4	1.02	4.30	4.22

It had been anticipated that the final curve might be of the form of an exponential function, but it was found that the results yielded a curve which, though of somewhat similar shape, differed markedly from a true exponential in that it did not tend asymptotically towards zero. In other words, while the greater part of the activating power of the light was

cut down by a relatively small thickness of chlorine, there appeared to be a residual effect which further concentration of chlorine was able to reduce only slightly.

In view of this result, it seemed desirable to obtain some additional confirmation. The possibility of stray light, or of light reflected from, or transmitted through, the tube sides was first investigated. When the light was stopped by placing a screen which just covered the aperture of the filter tube, it was noted that the reaction was completely arrested. Next, a very small aperture was used, so as to limit the beam to a fine pencil of rays along the axis of the tube and, so, to exclude any possibility of effects due to the side walls. The reaction values were thereby reduced greatly, but the ratios for different chlorine pressures were practically the same as before.

An attempt was then made to measure the velocity of the reaction by an independent method and, for this purpose, the Draper expansion was considered. This phenomenon, which is also known as the Pringsheim effect,

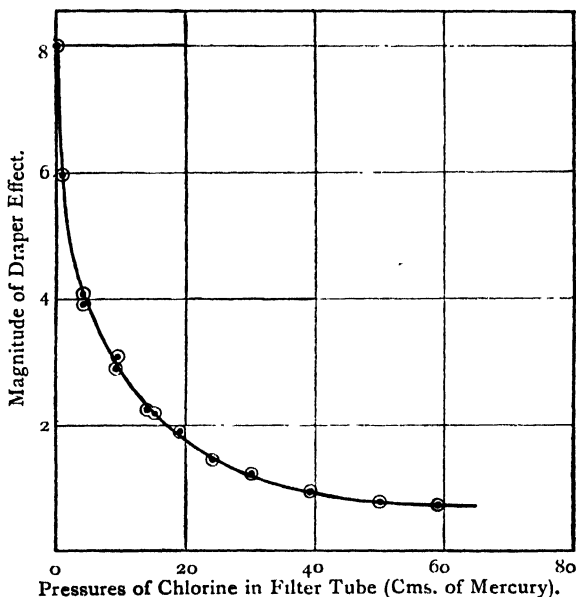


FIG. 3.—Draper expansions plotted against densities of filtering medium [chlorine gas].

is the sudden volume change which the mixed gases undergo at the instant of illumination. It has often been dealt with in the literature of the subject<sup>1</sup> and it is only necessary to say here that the magnitude of the expansion is proportional to the subsequent steady reaction velocity. Hence a measurement of the Draper effect may be used in place of the latter to determine the rate of activation of the chlorine. To observe the effect, the same actinometer was used and the initial index movements were magnified by a small lens. Since they were often of the order of an inch, a fair degree of accuracy could be obtained. Much greater speed in reading could of course be obtained, but the method had the drawback that between each exposure, the value of *S* altered slightly. Three exposures were given with each filter charge and the mean was taken. The results are tabulated below and also plotted in Fig. 3. It will be seen that there is a great similarity between the curves of Fig. 2 and of Fig. 3.

<sup>1</sup> Mellor and Anderson, *J.C.S.*, 1902, **81**, 414; also Norrish, *J.C.S.*, 1925, **127**, 2323.

TABLE II.

Pressure of Chlorine in Filter Tube (Cms. of Hg).	Mean Draper Effect in Inches.
59	·074
50	·080
39	·094
30	·124
24	·144
19	·180
14	·223
9	·290
4	·387
1	·505
0 (White Light)	·780
15	·22 (New charge given to actinometer)
9·5	·31
4	·41
1	·60

### Conclusion.

The result of this work has been to establish the form of the actinic absorption curves obtained by varying the concentration of the absorbing medium. It is not intended to give any theoretical discussion at present, since further work is in progress upon the "residual effect." Nevertheless, two points may be mentioned here.

In the first place, the results seem to indicate a greater ease of transmission by the chlorine than has been supposed. So far from 10 cm. of chlorine removing the activating power, even 45 cm. were found to be ineffective, but this of course may be due to the more intense nature of the source employed. Secondly, the shape of the curve is such as to disfavour the idea that only a narrow range of frequencies is effective in promoting activation, since an exponential curve would then have been expected. It would seem that in addition to those frequencies which chlorine gas is able to absorb readily, the activation may be produced by rays which pass through thicknesses of the order of 50 cm. and, then, produce an effect of about 10 per cent. of the full reaction velocity under white light.

In connection with this, we may compare the extinction coefficient obtained by Bunsen & Roscoe, namely 17·17, with this value of about 45. The difference is presumably due to the actinic power of the light from a tungsten arc being much richer than that of the coal gas flame employed by the above workers. Further, there seem to be peculiar phenomena connected with the influence of intensity upon absorption and Allmand<sup>1</sup> has quoted some unconfirmed figures from which it appears that a transmission factor may vary from 46 per cent. to 66 per cent. according to the nature of the light source.

While closing this paper, the author would like to express his indebtedness to Professor G. W. Todd for his kindness and help throughout the progress of the research.

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<sup>1</sup> Allmand, *Trans. Faraday Soc.*, 1926, 21, 521.

## THE RESIDUAL EFFECT IN THE ACTINIC ABSORPTION OF CHLORINE.

BY WILFRID TAYLOR, M.Sc., EARL GREY MEMORIAL FELLOW, AND  
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(*Communicated by* PROFESSOR G. W. TODD.)

*Received 10th December, 1926.*

In the preceding paper (see p. 31) some experiments were described in which white light, after being passed through a filter-tube of chlorine gas, was used to promote the chemical combination of a mixture of hydrogen and chlorine. The results seemed to show that as the chlorine concentration in the filter was increased, the actinic power of the emergent beam ceased to fall off rapidly and tended towards a limiting value which was not zero. It was felt that this justified further work upon the action of the filtering media in removing the activating power from a beam of white light; the present paper deals with some experiments, which have been carried out in continuation of the previous work, having as their object the investigation of the reality of this "residual effect." The tube previously used, which was 45 cm. long, was never filled at pressures greater than atmospheric. Increased concentrations of chlorine could therefore be obtained either by using longer tubes, or by employing greater densities; both of these methods were adopted. With regard to the latter, it was not convenient to use high gas pressures, but it was thought to be of some interest to obtain an equivalent result by the use of a liquid solvent in which the percentage of dissolved chlorine could be varied. There are, however, several points to take into consideration when using liquid solutions, the most important being the modification of the absorption spectrum.

Although the absorption of the activating radiation is the property under investigation, it is obvious that this will depend on the optical absorption; the relationship between the two is in itself worthy of study, but in the present case, it was only desired to examine whether strong solutions of chlorine having very nearly the same absorption spectrum as the gas, give rise to the "residual effect."

The solvent may modify the optical properties of the dissolved molecules by submitting them to high molecular fields<sup>1</sup> and a normal spectrum similar to that of a gas is only obtained when the solvent molecules have very low values for their electrostatic moments. The ideal solvent would be hexane, with a zero moment, but it was considered preferable to use a liquid in which there could be no chemical action with the chlorine even under intense illumination. Carbon tetrachloride was therefore selected. In addition to being chemically neutral, its molecular moment is not too high, being as 4.8 to 10 compared with water at 15° C. and, in addition, it permits of a rapid analysis being made to determine the strength of the solution.

<sup>1</sup> Victor Henri, "Structure des Molecules," Chap. II.

### Experimental Details.

The light system and actinometer were exactly the same as described in the paper referred to above, the light from a "Pointolite" lamp being concentrated by a lens, and relative reaction velocities were obtained in the same manner as before. Instead of a filter tube of chlorine gas, a plane walled glass cell was employed, the light having to pass through a depth of 3 cm. of liquid. This cell was equipped with a closely fitting glass cap to prevent evaporation since the solution was very volatile. We were thus able to pass a strong beam of white light through a known quantity of dissolved chlorine and to measure the actinic power of the emergent light in terms of the velocity of the reaction between hydrogen and chlorine in the bulb of the actinometer.

A saturated solution was made by passing a stream of chlorine from a cylinder through a tower of pure carbon tetrachloride. To obtain lower

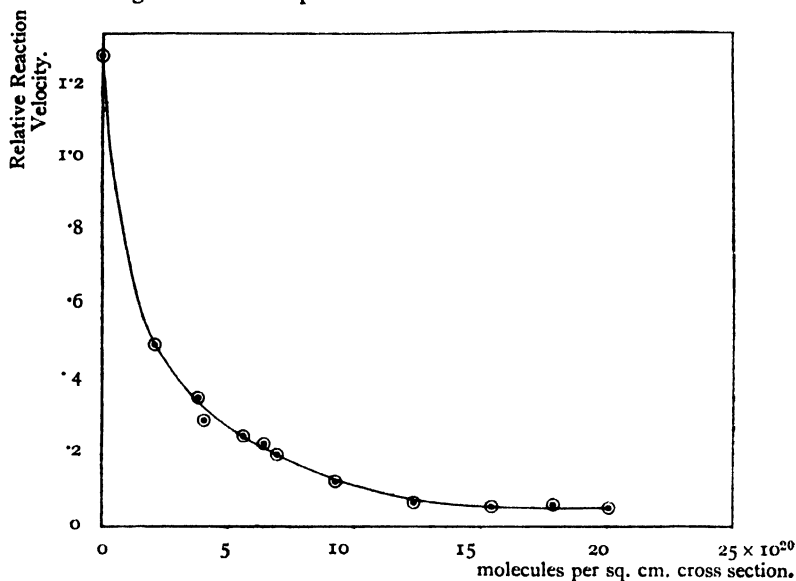


FIG. 1.

[Filter Tube of Chlorine Gas.]

concentrations, additional quantities of carbon tetrachloride were added to this stock solution. Unfortunately these solutions, especially those near the saturation point, were very unstable owing to evaporation and it was necessary to estimate the strength immediately after removing the cap of the filter cell at the end of an exposure. For this purpose 5 c.c. were transferred to a beaker and shaken with excess of aqueous solution of potassium iodide. The iodine liberated in the water layer was then titrated with  $N/10$  sodium thiosulphate and the shaking continued until all the chlorine and iodine had passed from the carbon tetrachloride into the water.

Another source of trouble lay in the tendency of some of the stronger solutions to become turbid, presumably owing to the internal liberation of chlorine. The turbidity could be removed by filtration and was always looked for carefully. In any case it may be observed that a cloudy liquid would decrease the intensity of the light transmitted and so would operate against the residual effect under investigation.

A whole range of solutions was taken in turn and the reaction induced in the actinometer was determined while each one occupied the cell. The results are set forth in Table I. In column (a) is given the estimated concentration of the chlorine solution in terms of the amount of  $N/10$  thio-sulphate required to titrate 5 c.c. of chlorine solution; in column (b) is given the number of chlorine molecules actually interposed per square centimeter of cross section of the beam; in column (c) is the corrected reaction velocity produced in the actinometer.

TABLE I.

(a).	(b).	(c).
0.0	$0.0 \times 10^{19}$	3.66
78.0	142.1 "	0.39
43.1	78.5 "	0.54
45.1	82.0 "	0.33
40.3	73.2 "	0.39
33.4	60.7 "	0.51
29.3	53.3 "	0.48
24.8	45.1 "	0.60
22.7	41.3 "	0.68
19.3	35.0 "	0.72
15.3	27.8 "	0.92
14.1	25.7 "	0.86
13.3	24.1 "	1.06
7.3	13.2 "	1.62
4.3	7.7 "	2.38
1.5	2.76 "	2.96

Having now completed this series, the effect of large gas concentrations was studied by means of a very long filter tube. In order to carry the experiments as far as possible, a glass tube of 159.5 cm. was used, having a diameter of about 5 cm., although the effective diameter of the light beam was cut down by a series of apertures, so that only the axial rays were employed. The ends were closed by plane glass plates sealed on with "picein" wax. The arrangement of gas supply, pump and manometer were the same as in the experiments with the short tube and are described in the previous paper. The effect of the new tube was in fact simply to extend the curve given in this paper to regions of greater chlorine concentrations.

The results of the experiments are given in Table II., and are illustrated in Fig. 1. Column (a) gives the pressures of the chlorine in the filter tube as read by the manometer, while in (b) these are expressed in terms of the number of chlorine molecules lying in the path of unit area of cross section of the beam, the temperature and barometric pressures being allowed for, and in column (c) are the reaction velocities.

It may be remarked that the readings were not taken in the above order, but always in a random selection of the pressure.

It seemed very important to estimate the error due to the viscous drag of the liquid in the index tube. During the course of a reaction, the index liquid moved so as to fill an additional length of about 40 cm. of millimetre bore tubing. Trial runs showed that no deviations from a constant velocity could be detected over this range, so that if the viscosity played any appreciable part, it could only do so by causing a steady rise of pressure in the bulb to compensate for the additional viscous drag.

TABLE II.

(a).	(b).	(c).
0.0 cm. Hg.	0.0 × 10 <sup>27</sup>	I'24
75.0 "	40.1 "	0.05
66.7 "	35.7 "	0.06
57.7 "	30.9 "	0.05
46.3 "	24.8 "	0.06
34.5 "	18.5 "	0.12
25.9 "	13.9 "	0.19
23.9 "	12.8 "	0.22
21.0 "	11.2 "	0.24
15.0 "	8.0 "	0.28
14.3 "	7.6 "	0.34
7.8 "	4.2 "	0.48

Taking the rate of reaction as the time rate of change of gas volume at constant pressure, it is found that the real reaction velocity is given by

$$K = u\pi a^2[1 + B], \quad B = \frac{\delta V \eta}{\pi a^4 p} u$$

where  $u$  is the observed velocity of the index,  $V$  the volume of the bulb,  $a$  the radius of the tube and the other symbols have their usual significance. Now since no reaction velocities had an index speed of more than 1 cm./sec., the numerical magnitude of  $B$ , on putting the values  $V = 16$  c.c. approx. and  $a = 0.75$  mm., is well below 0.001, and hence can be safely neglected.

### Conclusions.

All the curves obtained so far, although exhibiting certain differences as yet unaccounted for, agree in showing a "residual" effect, that is to say, the activating power of the light after passing through large concentrations of chlorine, is greater than would be expected were the light monochromatic and absorbed in accordance with an exponential law.

From an inspection of the curves, it appears that certain types of radiation present in ordinary white light, are only feebly absorbed by chlorine and, yet, are able to give rise to an appreciable amount of activation. It is claimed that these results, while at present rather of a qualitative nature, indicate that, by the use of this method, some information may be obtained concerning the specific activating power of the feebly absorbed frequencies. Further work is at present in progress.

The authors wish to regard their appreciation of the facilities and assistance afforded them by Professor G. W. Todd.

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# THE ELECTROSTATIC CAPACITY OF ALUMINIUM AND TANTALUM ANODE FILMS.

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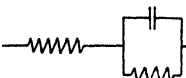
(Communication from the Staff of the Research Laboratories of the General Electric Co. Ltd., Wembley.)

Received 18th October, 1926.

## Introduction.

The electrostatic capacity of aluminium and tantalum anode films was thought to be worth investigation for two reasons. In the first place it was hoped to obtain some information about the rate at which the thickness of the film increases in order to interpret satisfactorily any results obtained and, generally, the increasing importance of the tantalum rectifier makes further theoretical knowledge necessary as a basis for design. The subject has been investigated by a large number of workers, but their almost unanimous neglect of the influence of frequency on the capacity and the great divergence of their results made further investigation desirable. Franchetti<sup>1</sup> measured the capacity of an aluminium anode at frequencies of 41 and 81 cycles per second and concluded that the capacity was independent of the frequency. Bairsto and Mercer<sup>2</sup> stated that "up to the present there is no evidence of the capacity of an aluminium condenser varying with the frequency," but they quoted neither figures nor experiments in support of this statement. A. H. Taylor<sup>3</sup> alone seems to have observed a change of capacity with frequency. We have found a marked change of capacity with frequency; the neglect of this change by previous workers may partly account for their discrepant results.

But there is another factor to be taken into account, namely, the meaning which is given to the phrase "equivalent capacity of an aluminium or tantalum anode." It has to be borne in mind that there is an infinite number of such equivalent capacities since it is possible to devise an infinite number of networks, each giving the same power factor as the aluminium or tantalum anode. Very few investigators have stated to what network they assumed the valve anode to correspond; in such cases we can only infer from their method of measurement what kind of network they assumed to be equivalent. McC. Gordon,<sup>4</sup> for instance, clearly supposes the anode to

be equivalent to a network of the form . A. L. Fitch<sup>5</sup>

<sup>1</sup> Franchetti, *Rev. Sci. Ind.* (1901), **33**, 121.


<sup>2</sup> Bairsto and Mercer, *Trans. Faraday Soc.* (1911), **7**, 1.

<sup>3</sup> A. H. Taylor, *Ann. Physik* (1909), **30**, 987.

<sup>4</sup> McC. Gordon, *Physical Rev.*, **24**, 60.

<sup>5</sup> A. L. Fitch, *Physical Rev.* (1917), **9**, 15

assumes that the anode is equivalent to a condenser with a double dielectric. Bairsto and Mercer<sup>1</sup> evidently assume an electrolytic condenser to be

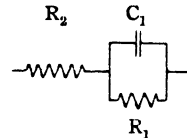
equivalent to . Now it is obvious that the equivalent

capacity of McC. Gordon cannot be the same at all frequencies, for example, as the equivalent capacity of Bairsto and Mercer and, therefore, it is only to be expected that values of gas film thickness deduced from McC. Gordon's measurements will differ from those of Bairsto and Mercer.

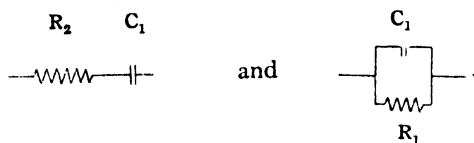
The only method of discriminating between all the possible networks is by making experiments over a fairly wide frequency range. If we have correctly pictured the construction of the anode films in our equivalent electrical network then the equivalent capacity will be independent of the frequency. We assumed for purposes of experiment that an electrolytic condenser (composed of two similar metal plates in an electrolyte) was equivalent

to the following simple electrical network, .

The series resistance is supposed to represent the resistance of the electrolyte; the capacities in shunt with resistances represent the leaky condensers at each electrode.

If the two electrodes are equal in area this reduces to 

which is the same as McC. Gordon's network; and has the advantage of containing, as special cases, the networks:



### Experimental Details.

A bridge method of measurement at audio-frequencies was chosen as being far more accurate than other methods, though it is admitted that this does not represent the conditions normally encountered by commercial rectifiers, which generally deal with alternations of the order of 50 cycles per second. The balancing network consisted of a variable mica condenser  $C_2$  (see Fig. 1) of extremely small power factor in series with a non-inductive resistance  $R_3$ ;  $R_4$  and  $R_5$  were resistances of 100 ohms. The valve oscillator was of normal type and was situated about eight feet from the bridge. No trouble was experienced through earth capacities or through influence on the bridge apart from the coupling coil. The leads were run through earthed lead pipes and an earthed screen was interposed between the oscillating coil and the coupling coil to the bridge. The frequency of the alternations was measured with a Campbell frequency bridge, the introduction of which into the circuit caused no detectable change in frequency.

For experiments with aluminium electrodes the form of cell used is shown diagrammatically below (Fig. 2). Two highly polished aluminium

<sup>1</sup> Bairsto and Mercer, *Trans. Faraday Soc.* (1911), 7, 1.

electrodes A and B screw into an ebonite tube, a third electrode which acts as a cathode is screwed in at C. In the first experiments on aluminium the cell was kept in a large constant temperature tank, but this was subsequently found to be unnecessary as the temperature of the cell did not vary

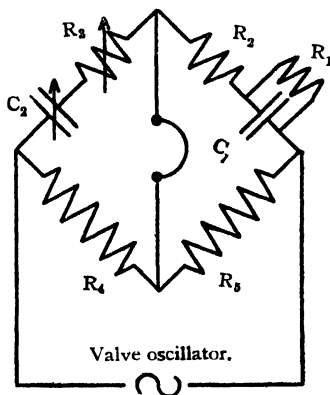


FIG. 1.

during the short time of taking observations. The full connections for forming the anodes and switching the cell into the bridge are shown. The inside diameter of the tube was 2.1 cm. and the distance between the electrodes was 6 cm.

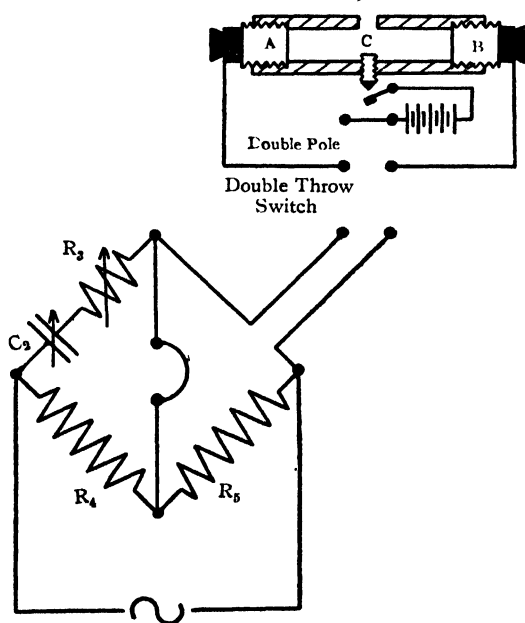


FIG. 2.

As tantalum was only obtainable in sheet form a different cell was used. It consisted of a lead cathode sandwiched between two tantalum plates which were insulated with wax except for two small areas, one on each plate, facing the lead cathode. Each area was 1.8 cm<sup>2</sup>.

It will be noticed that the bridge measurements of the cell were made with the formation current off. This was justified in three ways. In the first place, no discrepant results were obtained which could be ascribed to

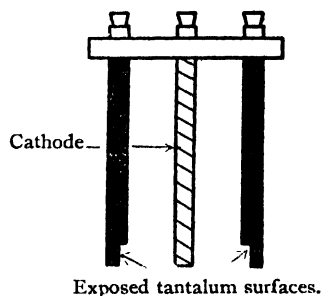


FIG. 3.

this cause or to the length of time during which the current had been switched off. Secondly, if the formation battery was placed in the telephone arm of the bridge, the point of balance was found to be unaffected by the presence or absence of the battery. Thirdly, the formation voltage was

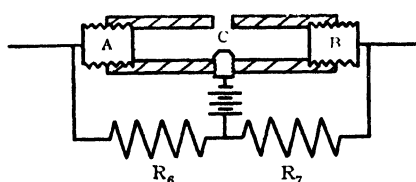


FIG. 4.

applied to the cell while bridge measurements were made by the circuit shown below, in which  $R_6$  and  $R_7$  were resistances of 100 ohms; again no difference in point of balance was detected when the battery circuit was opened or closed by a pendulum contact.

### Interpretation and Discussion of Results.

The method of experiment was simply that of recording the values necessary to balance out the electrolytic condenser with a non-inductive variable resistance and a variable condenser in series, over a range of audio frequencies. Since  $R_4 = R_5$  (see Fig. 1) the impedances of the balancing and electrolytic condenser networks must be equal if no sound is to be heard in the telephones.

If  $Z_1$  be the impedance of the network containing  $R_2$ ,  $R_1$  and  $C_1$ , and  $Z_2$  the impedance of that containing  $C_2$  and  $R_3$  then we have—

$$Z_1 = R_2 + \frac{1}{1/R_1 + j\omega_1 C_1} = R_2 + \frac{R_1 - j\omega_1 C_1 R_1^2}{1 + \omega_1^2 C_1^2 R_1^2}$$

and

$$Z_2 = R_3 + \frac{1}{j\omega_1 C_2}$$

$Z_1$  must equal  $Z_2$  as  $R_4 = R_5$ .

Hence equating real and imaginary parts we have—

$$R_3 = R_2 + \frac{R_1}{1 + (\omega_1 C_1 R_1)^2} \quad \dots \quad (1)$$

$$\frac{1}{\omega_1 C_2} = \frac{\omega_1 C_1 R_1^2}{1 + (\omega_1 C_1 R_1)^2} \quad \dots \quad (2)$$

If the electrolytic condenser really corresponds to the assumed network, these equations should hold at all frequencies. This was tested in the following way.  $1/\omega C_2$  (an experimentally determined quantity) was plotted against the frequency; two points were then taken from this curve and by

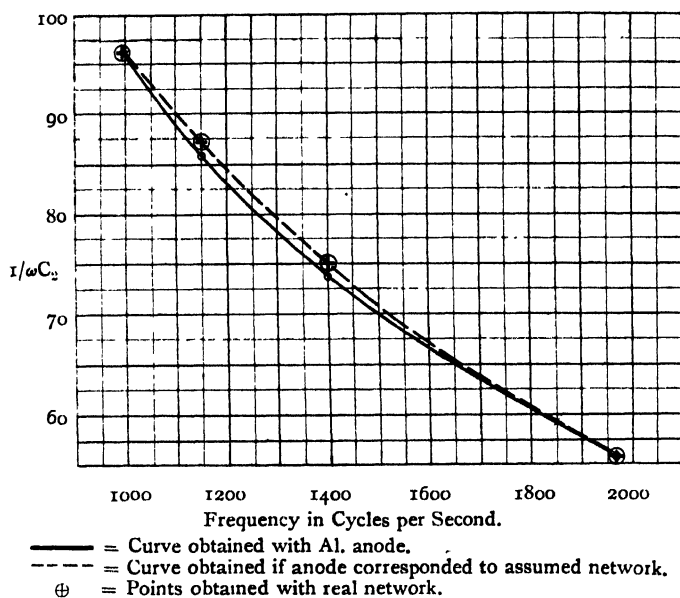


FIG. 5.

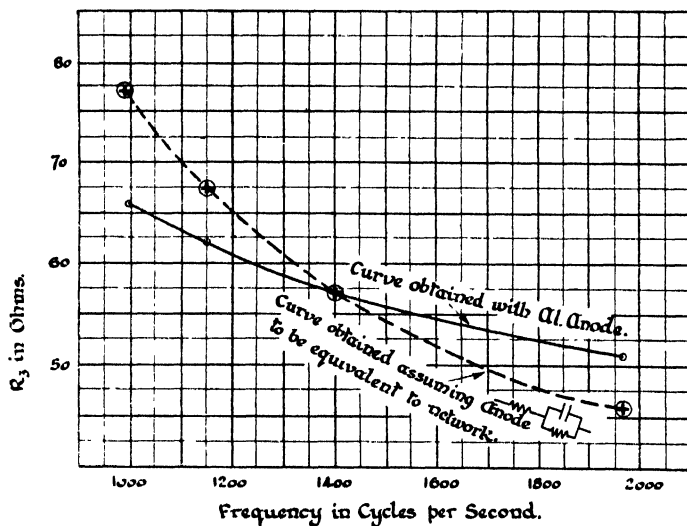


FIG. 6.

(2) a pair of corresponding values of  $C_1$  and  $R_1$  was determined. By substituting these numerical values and then plotting the expression  $\frac{\omega C_1 R_1^2}{1 + (\omega C_1 R_1)^2}$  against the frequency we should obtain the same curve.

Actually, as Fig. 5 shows, there is fair agreement between the curves given by  $1/\omega C_2$  and  $\frac{\omega C_1 R_1^2}{1 + (\omega C_1 R_1)^2}$ . But some measure of agreement is only to be

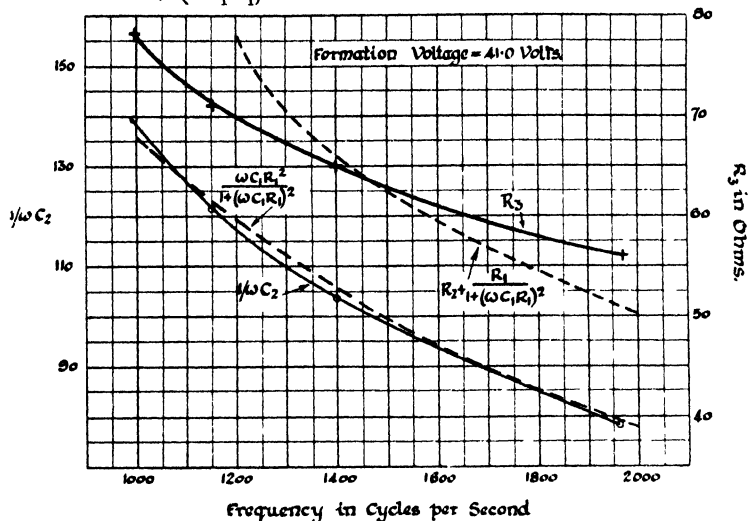


FIG. 7.

expected since we have assumed two coincident points. The real test comes when we substitute these values for  $R_1$  and  $C_1$  in equation 1, and plot the variation of  $\frac{R_1}{1 + (\omega C_1 R_1)^2}$  with frequency. We see from Fig. 6

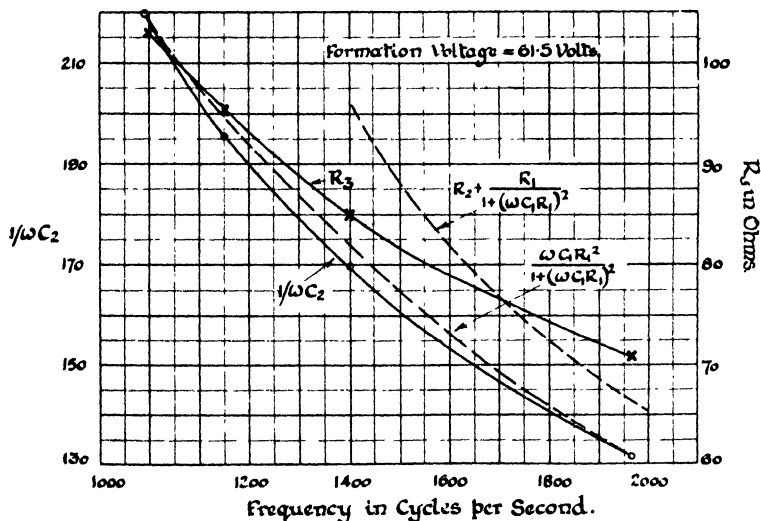
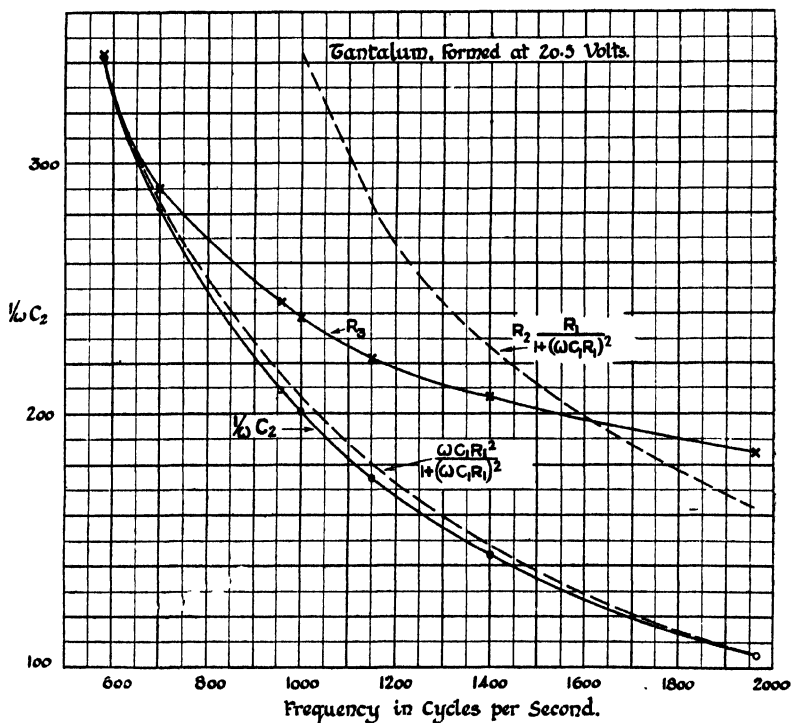
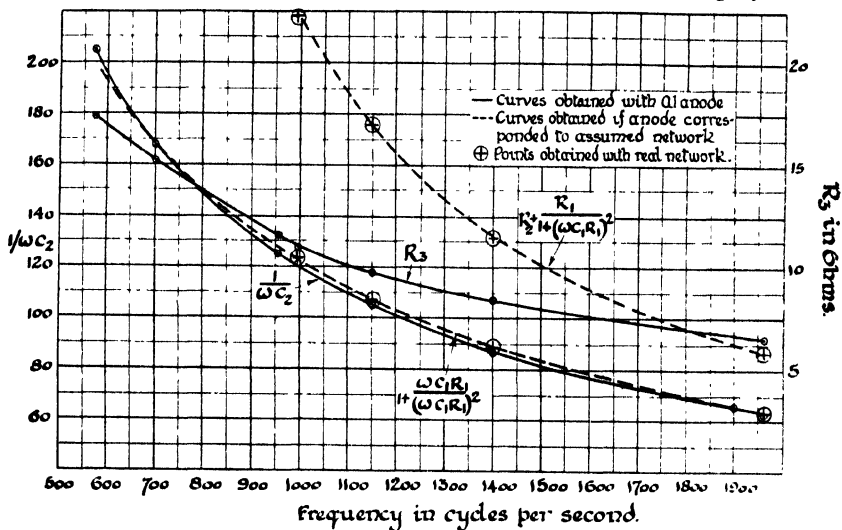


FIG. 8.

that the curve obtained is entirely different from that obtained by plotting  $R_3$  (an experimentally determined quantity) against the frequency. We assume one coincident point between these curves in order to obtain  $R_2$ .


(Figs. 7 and 8). Figs. 7 and 8 obtained with aluminium and a solution of ammonium phosphate (63 grams/litre) confirm Figs. 5 and 6. Figs. 9 and



FIGS. 9 and 10.

10 obtained with tantalum in dilute sulphuric acid of sp. gr. 1.285 at 18° C. show a similar disagreement between experiment and calculation.

It appears therefore that the aluminium and tantalum anodes do not behave as their equivalent networks have been calculated to behave; but we are not yet justified in concluding that the assumed network is not really equivalent to an electrolytic condenser, for in so doing we should be neglecting experimental errors. As a final test therefore, a real network with the calculated values of  $C_1$ ,  $R_1$  and  $R_2$  was substituted for the electrolytic cell; this real network gave the points marked  $\oplus$  in Figs. 6 and 9. It will be seen that these points lie on the calculated curves; we can only infer that the experimental and instrument errors are negligible and that therefore the assumed network does not correspond to an electrolytic condenser.

No doubt better agreement could be obtained by taking a more complicated network. A. H. Taylor<sup>1</sup> suggested that a valve anode might correspond to  and since such a network has five

undetermined constants it could be made to fit practically any curve, but it is doubtful whether such agreement would have much physical significance. It is better to be content with the statement that the dielectric on a valve anode is not homogeneous; this is confirmed by the experiments of Morse and Shuddemagen,<sup>2</sup> of Green,<sup>3</sup> and others who found that an electrolytic condenser has strong absorption.

### Variation of Equivalent Shunt Capacity and Resistance with Frequency.

With tantalum electrodes  $R_2$  is found to be very small; this is what might be expected since the value of  $R_2$  is comparable with the resistance of the electrolyte, which was dilute sulphuric acid. In this case it is instructive to calculate the equivalent shunt capacity and resistance at different frequencies to see what errors would be introduced by assuming them to be constant. Using the equations—

$$C_1 = \frac{C_2}{1 + \omega^2 C_2^2 R_2^2}$$

$$R_1 = \frac{1 + \omega^2 C_2^2 R_2^2}{\omega^2 C_2^2 R_2}$$

the results plotted in Fig. 11 were obtained.

These show that over this range of frequencies the actual discrepancies between readings and calculated values are not great.

### Rate of Change of Capacity.

Although our results show that it is difficult to attach any exact physical meaning to capacity measurements in the way hitherto employed, yet it is an undoubted fact, known for many years, that if measurements are made at any given frequency, the apparent electrostatic capacity is found to be an accurate function of the applied voltage, this capacity usually being taken as a measure of the thickness of the gas film.

All experiments previously made have dealt merely with final steady values of the capacity after the voltage has been applied for a sufficiently long time. It was thought interesting further to investigate the rate at

<sup>1</sup> A. H. Taylor, *Ann. Physik* (1909), **30**, 987

<sup>2</sup> Morse and Shuddemagen, *Proc. Amer. Acad. Arts. Sci.* 1909, **47**, 367.

<sup>3</sup> Greene, *Physical Rev.*, 1914, **3**, 264.

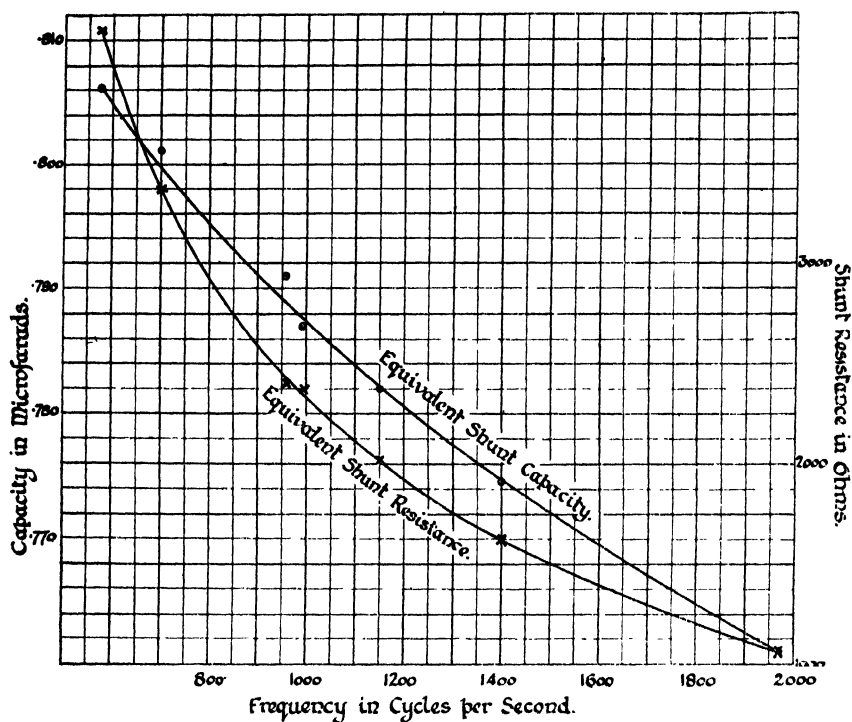


FIG. 11.

Frequency Cycles. ---- 1170. ——— 1945.

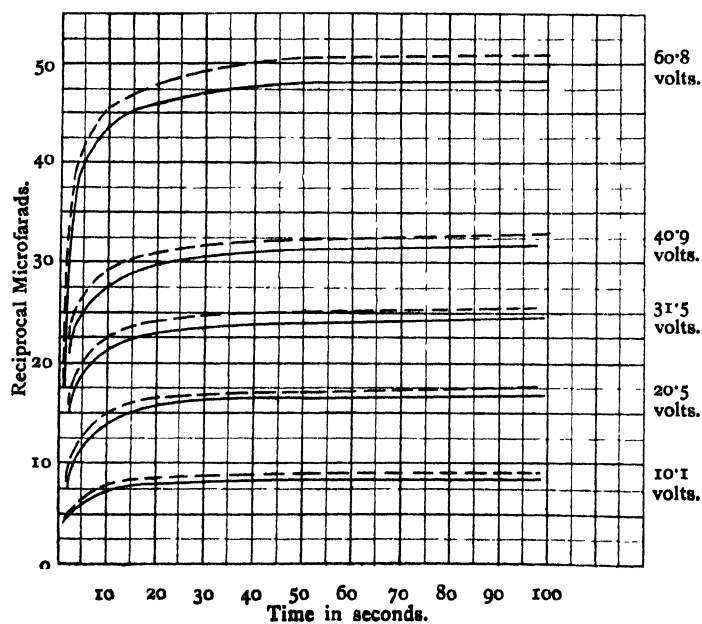


FIG. 12.

which the capacity attains its steady value. As this process is a very rapid one the device was adopted of applying the formation voltage for a succession of small periods and measuring the capacity (and resistance) necessary for balance after definite times, when the formation voltage was not in circuit. This was done by making connection with the applied voltage through an electrically released pendulum, the point of which in the course of its swing passed through a small pool of mercury, thus completing the circuit. The time intervals so obtained were measured by means of an electrically actuated needle in series with the pendulum-contact which made marks upon a smoked disc revolving at a known constant speed. The actual duration of each swing was 0.10 seconds. The cell used was of the same type as that used in the first part of the work, but in this case the area of the anode was 2.85 sq. cm. The solution was 100.4 grams/litre ammonium phosphate solution.

Readings were taken of the capacity of aluminium anodes with the following applied voltages—10.1, 20.5, 31.5, 40.9 and 60.8. At each point the bridge was balanced at two frequencies, namely 1945 and 1170 cycles per second, by means of a condenser and resistance in series.

In Fig. 12 the reciprocals of the capacity are plotted against the time during which the formation voltage has been applied, at both the high and the low frequencies. The reciprocals of capacity are preferred because they have more meaning when the impedances of the cells are considered and also because they show quite clearly the known law that the "Film thickness is proportional to formation voltage." The rate of growth, which appears at first sight to be approximately logarithmic, was found upon careful examination to show unmistakable deviations from a truly logarithmic curve, but so far no theory has been found which will mathematically fit the observed rate of growth.

### Summary.

It is shown conclusively that if an electrolytic condenser be assumed equivalent to a network of simple and calculable form, the values of the constituent parts of that network are not independent of frequency.

No simple network can be found which is an exact equivalent, though there is probably an infinite number of more complex networks possible. For this reason no exact physical significance, such as measurement of film thickness, can be attached to any values of capacity which may be obtained.

Experiments show that the reciprocal of the capacity of an aluminium anode increases to a steady value according to an approximately logarithmic law of growth.

# THE BEHAVIOUR OF THE QUINHYDRONE ELECTRODE IN SOLUTIONS OF NEUTRAL COPPER SULPHATE.

BY JASPER B. O'SULLIVAN, B.Sc.

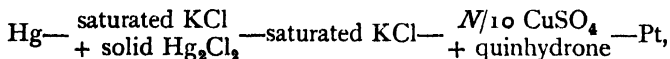
(Received 7th September, 1926.)

## Introduction.

In a previous paper<sup>1</sup> it was shown that, whereas in solutions of copper sulphate acidified with sulphuric acid the quinhydrone electrode gives a definite and steady potential, yet in solutions of the neutral salt, which are slightly acid by hydrolysis, the potential exhibits a pronounced drift with time. This was attributed to gradual coagulation of the colloidal particles of cupric hydroxide, produced by hydrolysis, whereby adsorbed acid was set free. It was alternatively suggested by Dr. Rideal that the potential drift might be due to autoxidation of the quinhydrone, catalytically accelerated by the copper salt, or to the formation of complexes between the copper ions and the quinhydrone or one of its constituents. It, therefore, seemed desirable to investigate the matter further, in order to determine, if possible, the true cause of the phenomenon.

## Experimental.

In the first place, it should be stated that determinations of the potential of the cell,



carried out over periods of several days, showed that it did not reach a constant value after two days, as had previously been thought, but continued to change very slowly even up to seven days.

To test whether the potential drift was due to autoxidation of the quinhydrone, the following experiments were performed. Firstly, a  $N/10$  solution of copper sulphate was prepared with well-boiled distilled water. This was introduced into the electrode vessels, a little solid quinhydrone added and the vessels were immediately and completely filled with the solution and closed, so as to prevent the access of air to the solutions. The values so obtained are given in columns A and B of Table I.

Secondly, a quino-quinhydrone electrode was employed. This was prepared by first shaking the solution to saturation with quinone and, then, with quinhydrone. Since the liquid was saturated with both constituents, gradual oxidation of the quinhydrone would merely cause some quinone to be precipitated, whilst more quinhydrone would go into solution; thus the potential of the electrode would remain unchanged. The values obtained are given in columns C and D. For column C, the solution was shaken for five minutes after the addition of each constituent, whilst for column D, ten minutes shaking was given after each addition.

<sup>1</sup> *Trans. Faraday Soc.*, 1925, **21**, 319.

Finally, some of the copper sulphate solution was shaken with solid quinhydrone for ten minutes and the electrode vessel was only partially filled. The values obtained are given in column E. For comparison, some of the original values (*loc. cit.*, p. 322) are given in column F. All times are taken from the introduction of the liquid into the vessel. The potentials are given to the nearest half millivolt.

TABLE I.

Time.	A. B.		C. D.		E.	F.
0 hr. 5 min.	- '2000 volt	- '2010	- '2700	- '2790	- '2020	—
0 " 10 "	- '2000	—	—	—	—	- '2005
0 " 15 "	- '2005	—	- '2720	—	- '2030	—
0 " 20 "	- '2010	—	—	- '2805	—	—
0 " 30 "	- '2020	- '2030	- '2725	—	—	—
0 " 40 "	—	- '2050	—	- '2815	- '2040	- '2020
1 " 15 "	- '2050	—	- '2745	- '2840	- '2050	- '2025
2 days	- '2150	- '2170	- '2820	—	—	- '2150
2 "	- '2145	- '2175	- '2815	—	—	- '2150
5 "	—	—	—	- '2920	—	—
5 "	—	—	—	- '2920	—	—
7 "	- '2250	- '2280	- '2920	—	—	—
7 "	- '2255	- '2270	- '2915	—	—	—

The above figures demonstrate that the potential drift is practically identical in all these cases, at any rate over the longer periods. Thus, it cannot be due to autoxidation of the quinhydrone.

The next set of experiments was directed to ascertaining whether the drift was due to the presence of solid quinhydrone, which might adsorb colloidal cupric hydroxide. The copper sulphate solution was shaken with quinhydrone and filtered before being introduced into the electrode vessels. (columns A and B of Table II.) A  $N/5$  solution of copper sulphate was diluted with an equal volume of a filtered solution of quinhydrone (columns C and D).

TABLE II.

Time.	A. B.		C. D.	
0 hr. 5 mins.	- '2035 volt.	- '1995	- '1965	- '1980
0 " 25 "	- '2040	- '2010	- '1970	- '1975
1 " 0 "	- '2045	- '2020	—	—
2 days	—	—	—	- '2045
2 "	—	—	—	- '2045
5 "	- '2160	—	- '2145	—
5 "	- '2165	—	- '2145	—
7 "	- '2255	—	- '2170	—
7 "	- '2255	—	- '2165	—

Thus the drift occurred even when the copper sulphate solution had never been in contact with solid quinhydrone, so that it could not be due to adsorption of cupric hydroxide by the latter.

Further, the explanation was not to be found in a spontaneous change in the copper sulphate solution, for such solutions which had been kept for a month or more gave approximately the same initial value as those which had been made up within the hour. Thus, the author's original suggestion was incorrect.

## 54 BEHAVIOUR OF THE QUINHYDRONE ELECTRODE

The next set of experiments consisted of a visual examination of the solution. 20 c.c. of *N/10* copper sulphate solution were shaken with 0.07 gm. of quinhydrone and filtered. This solution was used to fill a test tube, which was then corked (*solution A*).

0.20 gm. of hydroquinone was dissolved in 20 c.c. of *N/10* copper sulphate solution, and used to fill another test tube, which was likewise corked (*solution B*). This solution became slightly turbid almost at once.

After two days, there was a slight sediment in B, but A was clear. After a further five days, there was a distinct brownish sediment in B and a very slight sediment in A.

It thus became a matter of interest to determine whether quinone or hydroquinone alone would affect a copper sulphate solution in the same way that quinhydrone had been found to do. For this purpose, the following comparative experiments were carried out.

0.048 gm. of quinone was dissolved in 20 c.c. of *N/10* copper sulphate solution. After five days, 0.049 gm. of hydroquinone (the equivalent of the quinone previously added) was added, shaken for a minute and introduced into the electrode vessel (column A of Table III).

This experiment was repeated, except that the hydroquinone was first dissolved in the copper sulphate solution and the quinone was added after five days (column B). In both cases, a precipitate of quinhydrone was formed. The latter experiment was repeated, using the same quantities of hydroquinone and quinone, but 30 c.c. instead of 20 c.c. of the copper sulphate solution, so that no quinhydrone was precipitated (column C).

TABLE III.

Time.	A.	B.	C.
5 mins.	- '2050 volt.	- '2390	- '2365
10 "	- '2055	- '2405	- '2375
40 "	- '2060	- '2400	- '2380
2 days	- '2115	- '2420	- '2385
2 "	- '2125	- '2420	- '2385
7 "	- '2280	- '2470	- '2480
7 "	- '2275	- '2470	- '2480
9 "	—	- '2495	—

Thus, it is seen that solution A, which had stood in contact with quinone, showed practically the same initial potential as a freshly prepared solution, *viz.*, 0.2050 volt instead of 0.2010 volt, whereas solutions B and C, which had stood with hydroquinone, gave initial values differing from this by about 3 centivolts. We may, therefore, conclude that it is hydroquinone, and not quinone, which affects the copper sulphate solution. Thus it would appear that the phenomenon is due, in some way, to reduction of the copper sulphate. This could take either of two courses; firstly, reduction to the metallic state with liberation of sulphuric acid, or secondly, reduction to cuprous sulphate with liberation of half as much acid. But, from the known values for the electrode potentials of these processes, it is clear that the quantities of acid produced by the time that equilibrium was attained would be much too small to have any appreciable effect on the  $P_A$  of the solution. Also, these reactions would, in all probability, take place with great rapidity.

Thus, there remains the possibility that a little cuprous sulphate is

formed by reduction and that this subsequently reacts in such a way as to disturb the cupri-cupro equilibrium, so that more reduction can take place. Now, it is known that cuprous oxide is precipitated, owing to hydrolysis, from solutions of cuprous sulphate, even when the latter are very dilute, thus providing the condition necessary for further reduction of the cupric sulphate.

It, therefore, seemed desirable to investigate the sediments formed from solutions of copper sulphate and quinhydrone or hydroquinone.

12.5 gm. of crystallised copper sulphate were dissolved in about 500 c.c. of water. 1.65 gm. of quinhydrone were shaken with about 400 c.c. of water and filtered. The two solutions were mixed in a litre flask, which was then completely filled up with water, and stoppered (solution C).

13.75 gm. of copper sulphate were dissolved as before, and mixed with a filtered solution of 5.64 gm. of hydroquinone in an 1100 c.c. flask, filled up with water and stoppered (solution D).

After five days, a considerable sediment had formed in each case. The sediments appeared to be brown. They were filtered through Gooch crucibles, washed with water, alcohol and ether, dried in a steam oven and weighed; then ignited and reweighed; finally extracted with dilute nitric acid, and their copper content determined colorimetrically.

These experiments were repeated, using 13.75 gm. of copper sulphate and 1.03 gm. of quinhydrone in a total volume of about 1100 c.c. (solution C'), and 12.5 gm. of copper sulphate with 5.0 gm. of hydroquinone in a total volume of about 1000 c.c. (solution D').

TABLE IV.

	Solution C.	Solution C'.	Solution D.	Solution D'.
Weight of sediment . . .	.0081 gm.	.0069	.0086	.0102
Weight of ignited sediment	.0000	.0005	.0023	.0021
CuO (colorimetric) . . .	.0003	.0004	.0018	.0024

Thus, whilst the quantity of organic precipitate was of the same order in both cases, the quantity of copper in the precipitate was very different, being greater in that case in which the reducing power is greater. Now, if the precipitated copper were in the form of a complex with the organic matter, we should expect that it would form a constant proportion of the precipitate whether quinhydrone or hydroquinone were used. It would, therefore, seem probable that the copper is precipitated by hydrolysis of the cuprous sulphate and that the organic matter in the precipitate is a tarry oxidation or decomposition product; the latter is also formed, though more slowly, in acid solution, but then contains no perceptible quantity of copper. An attempt was, therefore, made to extract the organic matter from the precipitate. It was found to be insoluble, or only slightly soluble, in alcohol, ether, benzene, chloroform, carbon bisulphide, acetone and petroleum ether, but completely soluble in moist pyridine or sodium hydroxide solution. The latter solvent also extracted the copper, so that it was not possible to discover in what condition this was present.

### Conclusion.

It has been shown that the drift of potential exhibited by a quinhydrone electrode in solutions of neutral copper sulphate is not due to oxidation of

the quinhydrone, nor does it appear to be due to the formation of complexes between the copper ions and the organic material. The precipitates formed from copper sulphate and quinhydrone or hydroquinone have been examined and found to contain a varying proportion of copper, which is greater when the reducing action is greater. It would, thus, appear that the potential drift and the gradual production of a precipitate containing copper, are due to the formation, and slow hydrolysis, of cuprous sulphate.

The author wishes to express his thanks to Dr. H. Sand for his continued interest in the above investigation and for his valuable advice and suggestions during its progress.

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### REVIEWS OF BOOKS.

**The Problem of Physico-Chemical Periodicity.** By E. S. HEDGES and J. E. MYERS. (Arnold, pp. 95. Price 7s. 6d. net.)

This is a very useful monograph on a subject of distinct interest, written by authors who have themselves, during the last two or three years, made contributions of value to the study of the phenomena which they are discussing. After a brief introduction, chapters are devoted to *static periodicity* (variation of some property as a periodic function of a magnitude other than time or distance, such as temperature or concentration), *periodic structures* (where distance is the unidirectionally varying magnitude) and *periodic chemical reactions* (rate of change a periodic function of time). The well-known hydrogen periodic reaction receives special treatment, and there is a chapter of much interest on periodic electrochemical phenomena. The treatment appears to be as complete as the limits of space permit, although mention of the work of Grube and Reuss on the cathodic deposition of copper from copper sulphate, gelatine solutions seems to have been omitted. The reviewer would also suggest that the observations of Plotnikow referred to on p. 62 require confirmation, to say the least.

It will be obvious that the experimental material discussed is of the most diverse nature; this impression is enhanced by a closer study of the actual examples described—Liesegang rings, the hardness of metals as a function of the amount of work done on the metal, the opacity of blood serum as a function of added sodium chloride concentration, the rate of solution of metals, the luminosity of phosphorus, the rate of adsorption of gases, and many others. Under these circumstances it is courageous of the authors to have attempted, as they have, the elucidation of a cause, or perhaps better, the discovery of a factor, common to all these varied phenomena. Their view, briefly, is that the common factor determining periodicity is the existence in the system in question of some form or another of matter in a metastable condition. This suggestion is made by them with diffidence, and they would be the first to agree that it requires much working out, experimental and otherwise. For the time being they marshal in its support, in the last chapter of their book, a whole series of facts and considerations, the cumulative effect of which is certainly far from negligible.

Professor Donnan has written an appreciative foreword.

A. J. A.

## ON THE VELOCITY OF CHEMICAL REACTION IN THE SILENT ELECTRIC DISCHARGE.

By G. A. ELLIOTT, RAMSAY MEMORIAL FELLOW; S. S. JOSHI and R.  
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26th January, 1927.*

*(Communicated by PROFESSOR F. G. DONNAN.)*

Despite the numerous investigations that have been made on chemical changes produced by an electric discharge through a gas, no satisfactory general hypothesis has yet been suggested to describe the mechanism of such changes. In this communication an hypothesis is advanced which leads to an expression relating the velocity of such chemical reactions to the gaseous pressure and to the electrical factors which determine the discharge.

The fundamental idea from which this expression is derived was suggested by Professor F. G. Donnan, F.R.S. It is that the velocity of such chemical reactions might be associated with the number of collisions between ions and gas molecules in which the energy of the ion is equal to, or exceeds, a certain critical value. This value can be regarded as the critical energy of activation associated with the particular reaction concerned. According to the collision theory of chemical reaction, the rate of chemical change in a gas is a function of the kinetic energy of the constituent particles; it is immaterial whether the kinetic energy is of thermal or electrical origin. The concept of critical activation energies may therefore be applied to chemical reactions in which the energy necessary to effect chemical change is of electrical origin. It will be assumed, in order to simplify the discussion, that the radiations arising in the discharge produce no chemical changes.

Under normal conditions the number of charged particles existing in a gas is known to be very small.<sup>1</sup> When a gas is subjected to an electric field the energy acquired by the ions during their free paths increases with the field strength. When this energy is equal to, or greater than, a certain critical value, known as the ionisation potential when expressed in volts, new ions are produced by collision and the number of charged particles in the gas increases rapidly. Since the increase in the average kinetic energy of all the particles in the gas depends on the number of ions and on the field strength, no appreciable chemical change may be anticipated until ionisation by collision occurs. This deduction is in agreement with experimental observation. When ionisation by collision takes place the electrical conductivity of the gas increases markedly and the gas is usually seen to glow.

<sup>1</sup> Harms., *Physikal. Zeit.*, 1902, 4, I, 11.

Consider 1 c.c. of gas, at a pressure  $p$ , which is subjected to the discharge for a small time period,  $T$ . If  $N$  is the number of ion pairs per c.c., and  $v$  is their average velocity in the direction of the electric field, then  $2NvT$  is the total ionic path traversed while the gas is subjected to the discharge. An ion which travels a distance  $x$  cms., in the direction of the field,  $E$ , acquires an energy  $Eex$  due to the field, where  $e$  is the ionic charge. If the critical activation energy for the reaction concerned is  $V_0e$ , then  $x_0$ , the corresponding critical ionic path, is equal to  $V_0E^{-1}$  cms.

According to classical kinetic theory, which is assumed valid under the conditions obtaining in the discharge,  $c$ , the number of collisions of an ion per centimetre of its path which terminate free paths equal to or greater than  $x_c$  is given by

$$c = C \cdot e^{-\frac{x_c}{l}} = C \cdot e^{-\frac{V_0}{lE}}$$

where  $C$  is the total number of collisions per centimetre of ion path, and  $l$  is the mean free path of the ion. Therefore the number of molecules of gas chemically changed, per c.c. in time,  $T$ , is

$$2NvT \cdot C e^{-\frac{V_0}{lE}}$$

and  $K$ , the velocity of reaction or the number of molecules changed per second, is given by

$$K = 2Nv \cdot C e^{-\frac{V_0}{lE}} \quad (1)$$

Since  $C$ , the number of collisions per centimetre of ion path is proportional to the pressure,  $p$ , it may be expressed by

$$C = kp$$

where  $k$  is a constant. Substitution of this expression for  $C$  in equation (1) gives

$$\frac{K}{p} = 2k \cdot Nv \cdot e^{-\frac{V_0}{lE}} \quad (2)$$

In order to apply this equation to experimental results, it is necessary to know the manner in which  $Nv$  varies with  $p$  and  $E$ . Equation (2) may then be used to calculate  $V_0$ , the critical energy, from values obtained experimentally for  $K$ , the initial velocity of reaction at various pressures and in a constant field,  $E$ . It is necessary to identify  $K$  with the initial velocity of reaction, since the nature of the gas will have changed after the commencement of the reaction and, therefore,  $Nv$  and  $l$  will have different values.

In many experiments on the chemical change produced in a gas by the action of an electric field sustaining ionisation by collision, it is found convenient to enclose the gas in an insulating envelope of glass or silica, whereby the gas is separated from contact with the metal electrodes. By this means any possibility of the formation of metallic arcs, or of specific catalytic action by the metal electrodes, is obviated. A typical example of such a device is the familiar Siemen's Ozoniser in which the insulating envelope and the electrodes are concentric cylinders. It is now proposed to discuss briefly the application of equation (2) to experiments carried out in this type of discharge vessel.

Such a discharge vessel can be considered as a system of three capacities in series, two associated with the dielectric walls and the third

with the annular space containing the gas.<sup>2</sup> A current will flow through the ozoniser if an alternating potential,  $V$ , is applied to the electrodes and, if this potential exceeds a certain value, ionisation by collision will occur in the gas. The conductivity due to the ions in the gas may be represented by the inverse of a resistance term shunting the third condenser. From known values of  $V$ , of  $P$ , the power developed in the gas, of  $I$ , the total current and of the frequency of alternation, it is possible by vectorial analysis to evaluate  $V_g$ , the r.m.s. potential across the gas space, and  $i$ , the r.m.s. value of the current carried by the ions.<sup>2</sup> If  $d$ , the width of the annular space, is small compared with the radii of the walls, then  $E$ , the field in the gas, is at any instant approximately uniform and its r.m.s. value is given by  $V_g d^{-1}$ . It may be mentioned that the ratio  $V V_g^{-1}$  is determined by the dimensions of the ozoniser and by the nature of the gas.

The current  $i$  per square centimetre carried by the gas can be expressed in the form familiar in electrolysis,

$$i = (U_+ + U_-) Ne$$

where  $U_+$  and  $U_-$  are the velocities of the positive and negative ions respectively, in the field  $E$ , sustaining the current  $i$ . Therefore

$$i = 2vNe$$

and

$$Nv = i/2e$$

where  $v$  is the mean velocity of the ions. Hence equation (2) may be written:

$$\frac{K}{p} = \frac{k}{e} \cdot i \cdot e^{-\frac{V_0}{iE}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now  $l$ , the mean free path of the ions, is equal to  $\frac{1}{C} = \frac{1}{p k}$ , and substitution in the above equation gives

$$\frac{K}{p} = \frac{k}{e} \cdot i \cdot e^{-\frac{p k V_0}{E}}$$

which may be written

$$\frac{k V_0}{E} = \frac{1}{p} \left( \log \frac{k}{e} + \log i - \log \frac{K}{p} \right) \quad . \quad . \quad . \quad (4)$$

In this latter form the equation may most readily be tested by experiments carried out with a constant field,  $E$ . For then  $\frac{k V_0}{E}$  is constant and the expression on the right, in which all the quantities may be determined, should also be independent of pressure.

In some experiments carried out in these laboratories it has been shown that the conduction current,  $i$ , measured for a constant value of the field on the gas, does not vary greatly over a limited range of pressures. For this case therefore we may write:

$$p \cdot \frac{k V_0}{E} = A - \log \frac{K}{p} \quad . \quad . \quad . \quad . \quad (5)$$

where  $A = \log \frac{k}{e} + \log i$ , and is constant.  $\log \frac{K}{p}$ , and  $p$  should therefore

<sup>2</sup> Warburg, *Ann. Physik* (1909), 28, 1-17; Lunt, *Phil. Mag.* (1925), 49, 1238

be linearly related ( $E$  constant); this conclusion has been experimentally confirmed.

It is interesting to consider an alternative expression in which the product  $N\bar{v}$  is expressed as a function of  $P$ , the power developed per c.c. in the gas, which is equal to the product of the field strength and the ionisation current per square centimetre.<sup>3</sup> That is  $P = E\bar{i}$ ; consequently, substitution of this expression in equation (3) gives

$$\frac{K}{P} = \frac{k}{e} \cdot \frac{P}{E} \cdot e^{-\frac{V_0}{E}} \quad (6)$$

Equations (4) and (6) thus relate in a most general way the velocity of reaction and the critical activation potential to the gas pressure, the mean free path of ions producing activation and the electrical factors determining the discharge.

In conclusion the authors desire to express their sincere thanks to Professor F. G. Donnan, F.R.S., for his active interest and valuable criticism during the development of this theory.

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<sup>3</sup>An account of the procedure appropriate to the determination of the power developed in the gas is shortly to be published by one of the authors (R. W. L.).

## THE ACTIVATION OF HYDROGEN IN THE ELECTRIC DISCHARGE.

BY G. A. ELLIOTT, RAMSAY MEMORIAL FELLOW.

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26th January, 1927.*

*(Communicated by PROFESSOR F. G. DONNAN.)*

Numerous observations have been made recently of the formation by both electrical and chemical methods of abnormally active forms of hydrogen. The results of this work indicate the existence of two main varieties of active hydrogen. The first, monatomic hydrogen, was discovered by Langmuir,<sup>1</sup> who immersed an electrically heated tungsten wire in hydrogen at pressures of not more than a few centimetres of mercury. The abnormal heat conductivity of the gas under such conditions was shown to be due to the dissociation of the hydrogen molecules. It was found that the resulting hydrogen atoms possessed many remarkable properties; they reduced sulphur, phosphorus, and arsenic to the corresponding hydrides at ordinary temperatures, were very readily adsorbed on surfaces and easily recombined with evolution of heat to form diatomic hydrogen. For example, although the hydrogen atoms could be condensed at the temperature of liquid air, on warming, diatomic molecules only were evolved.

<sup>1</sup> *J. Amer. Chem. Soc.*, **34**, **36**, **37**, and **38**.

A second active modification of hydrogen is the triatomic variety whose existence was first clearly indicated by the work of J. J. Thomson.<sup>2</sup> It would be reasonable to suppose that this substance is more readily formed at higher pressures than is monatomic hydrogen and, hence, it has been customary to refer to any active modification of hydrogen formed at pressures approaching atmospheric as triatomic hydrogen or "hyzone." Wendt<sup>3</sup> first recorded the formation of active hydrogen at ordinary pressures. He obtained it by the action of  $\alpha$  rays from radium emanation on pure hydrogen and, subsequently, by other methods.<sup>4</sup> Wendt and his co-workers found that their active hydrogen possessed the following properties which distinguish it from monatomic hydrogen:—

It is not strongly adsorbed on surfaces, will survive passage through a plug of glass-wool and is formed at higher pressures. Also it may be condensed in and evaporated from liquid air without loss of activity. In addition they state that it spontaneously decomposes after a time interval of the order of one minute, while recent work by Bonhoeffer<sup>5</sup> has shown that the half-life period of monatomic hydrogen is one-third of a second only.

Wendt,<sup>3</sup> Venkataramaiah,<sup>6</sup> and others, obtained active hydrogen electrically by methods involving the use of discharge vessels of the wire-in-cylinder and Siemen's ozoniser types, as well as by various arc discharge methods. This pioneer work has been entirely of a qualitative character, and the present investigation was conceived as an attempt to place this subject on a basis of quantitative experiment.

It was clear that for work of this character an accurate knowledge of the electrical factors concerned would be necessary. The electrical arrangements hitherto used for the production of active hydrogen have in all cases been of a somewhat indefinite character. The customary source of high voltage has been either an induction coil or a transformer fed with alternating current; while, in general, electrical measurements have been made in the primary circuits only. The types of discharge vessel most suitable for subjecting a gas to measurable electrical conditions are the wire-in-cylinder form based on the visual corona tube, and the Siemen's ozoniser. For this reason the work described below has been carried out with vessels of these two types. The wire-in-cylinder corona tube possesses the advantage that it may be operated with stationary potentials so that it is unnecessary to make measurements of frequencies and wave forms. There is, however, a certain limiting voltage beyond which the discharge becomes unstable; the corresponding limiting field that can be applied to the gas is equal to its dielectric strength, which is a function of the gas pressure.<sup>7</sup>

The discharge in a Siemen's ozoniser is much more stable and there would appear to be no limit to the strength of the field to which the gas may be subjected. In a Siemen's ozoniser the electrodes are separated from the gas space by the walls of glass or other insulator of which the vessel is constructed. A discharge can only be maintained, therefore, with the use of alternating potentials.

Preliminary experiments have shown that the fields obtainable using wire-in-cylinder electrodes are insufficient to produce active hydrogen

<sup>2</sup> *Phil. Mag.*, 1912, 24, 241.

<sup>3</sup> Duane and Wendt, *Physical Rev.* [2], 7, 689-691.

<sup>4</sup> Wendt and Landauer, *J. Amer. Chem. Soc.*, 42, 930 (1920), *et seq.*

<sup>5</sup> *Z. physikal. Chem.*, (1924), 113, 199.

<sup>6</sup> *Proc. Sci. Assoc., Visianagram*, 1922, *et seq.*

<sup>7</sup> Cf. F. W. Peek, "Dielectric Phenomena in High Voltage Engineering." McGraw Hill, 1915.

in measurable amount. Consequently, the bulk of the work described in this paper relates to discharge tubes of the Siemen's ozoniser type.

### General Experimental Arrangements.

Pure hydrogen was prepared by the electrolysis between platinum electrodes of a solution of barium hydroxide. The cell was water-cooled and adequate arrangements were provided for the separation of the products of electrolysis. With this apparatus the maximum rate of production of hydrogen was approximately three litres per hour. The gas was purified by passage over anhydrous calcium chloride, hot platinised asbestos to remove oxygen, potash purified by fusion with a little potassium permanganate and, finally, over a layer four feet long, of pure phosphorus pentoxide. This purifying train was evacuated as completely as possible before filling with hydrogen and the apparatus was left in use for several days before commencing experiments. For qualitative work and where a rate of flow beyond the capacity of the electrolytic cell was required, electrolytic hydrogen from cylinder was utilised. The cylinder hydrogen was, however, passed through the above-mentioned purifying train before use.

The supply of direct current at high voltages for experiments with the wire-in-cylinder discharge tube, was obtained by rectifying the output from an induction coil used as a transformer. The primary circuit was fed with alternating current at 400 cycles per second. A Kenotron valve was used as rectifier and the pulsating current so obtained was smoothed by means of a suitable condenser and choke coils. This unit delivered a maximum line voltage of 70 kilovolts.

For the ozoniser experiments the high tension alternating current was obtained from a transformer with a closed iron circuit or from a large induction coil used as a transformer. Two generators giving 80-200 volts at 400 and 85 cycles per second respectively supplied the requisite primary current. Intermediate frequencies were obtained by varying the speeds of rotation of these machines.

*Electrical Measurements.*—Voltages were measured by means of a Kelvin-White electrostatic voltmeter reading from 0 to 10 or 20 kilovolts, r.m.s. The voltmeter was connected directly between the two electrodes of the discharge tube.

When alternating potentials were used the power expended in the gas was measured by a method involving the use of a wattmeter of dynamometer pattern which was connected in the primary circuit. The power developed in the discharge is given by the difference between the wattmeter readings when the discharge is passing through the gas and when, other arrangements being unaltered,<sup>8</sup> the two electrodes of the discharge vessel are connected together and to the high voltage terminal of the transformer. It was necessary to make small corrections to the wattmeter readings for the copper losses in the transformer, since these vary with the load.

The principal frequency of the alternating current was calculated from the speed of rotation of the generator shaft, under the conditions of the experiment which was in progress, and from the number of poles in the alternator field. It must be understood that the frequency so determined is

<sup>8</sup> The normal arrangement was such that the outer electrode of the discharge tube and also one of the output terminals of the transformer were earthed.

the fundamental frequency only. No apparatus was available for the determination of wave forms.

### Experiments with Wire-in-Cylinder Corona Tube.

In the form finally adopted the wire-in-cylinder corona tube consisted of a silver<sup>9</sup> cylinder (8 inches long, 1 inch internal in diameter) which was highly polished on its inner surface and provided with a water-jacket for cooling purposes. The ends were belled out and ground to fit two glass end-pieces (see Fig. 1). The joints were lubricated with metaphosphoric acid. The axial wire was of silver (36-40 s.w.g.), and was suspended from

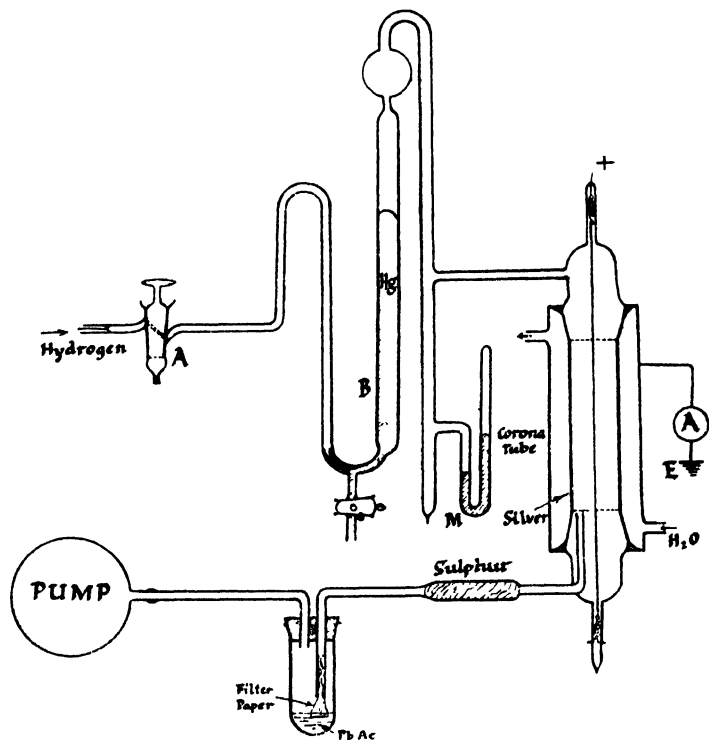


FIG. 1.

small platinum hooks sealed into the glass. The wire was stretched to a tension of about 10 g. weight, by means of two small steel springs placed at its ends. The apparatus was tested under vacuum for forty-eight hours and was found to be gas-tight. The inner wire was the positive electrode when stationary potentials were used. The outer electrode was connected through a milliammeter to earth.

The highest voltage which could be applied to this apparatus was 7500 volts. Hydrogen was streamed through the discharge at atmospheric pressure and then passed over a layer of sulphur which was placed as near to the end of the discharge tube as possible. The presence of hydrogen

<sup>9</sup> Wendt and Landauer have stated that silver and also certain other metals have no decomposing action on active hydrogen (*J. Amer. Chem. Soc.* (1922), **44**, 510).

sulphide in the issuing gas indicated the formation of active hydrogen. Hydrogen sulphide was detected by the blackening of lead acetate paper, over which the gas finally passed. It was found that no blackening of the test-paper could be detected when the discharge was excited with stationary, or with alternating, potentials (at 400 ~ and at 85 ~). The results were also negative when interrupted current was supplied by means of an induction coil with mercury break. Some experiments were also made at reduced pressures, with the apparatus shown in Fig. 1. The maximum rate of flow of the gas was of the order of 15 litres per hour at the pressure obtaining within the discharge tube. The pressure was varied from 1.5 to 10 cm. Hg. Very faint blackening of the test-paper could be detected in a period of about 1 hour, indicating the formation of minute traces of active hydrogen. Further work in this direction has been postponed on account of the very small yields of active hydrogen that have been obtained.

### Experiments with Discharge Tubes of Siemen's Ozoniser Type.

1. *At Atmospheric Pressure.*—In these experiments various discharge vessels were used whose gas spaces varied in thickness from 1.5 to 5 mm. The discharge was excited by alternating current at 85 and 400 cycles per second. The danger of fracturing the vessels limited the maximum voltage which could be applied to 10-15 kilovolts r.m.s. The volume enclosed between the end of the discharge tube and the detecting agent was never

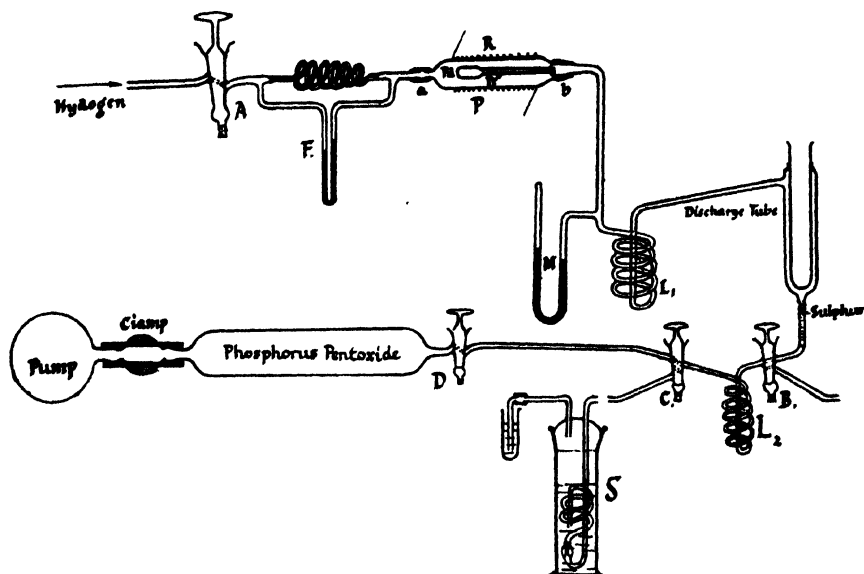


FIG. 2.

more than 3 c.c. so that with a rate of flow of electrolytic hydrogen of 3 litres per hour the time required for the gas to pass from the discharge to the reagent was approximately 3 seconds. At higher rates of flow cylinder hydrogen was used. The tests for activity were made with sulphur, very dilute acid permanganate, potassium nitrate solution and with tungstic oxide as reagents. No reduction was detected except in the case of sulphur.

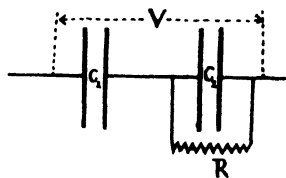
In this experiment pure electrolytic hydrogen was used and, after a continuous run of 5 hours' duration, a very faint indication of the formation of sulphuretted hydrogen was obtained.

2. *Experiments at Reduced Pressures.*—A series of qualitative experiments was next carried out at reduced pressures using the ozoniser of 1.4 mm. annular space which is shown in Fig. 2. The arrangement for admitting hydrogen to the discharge tube at reduced pressures is shown in Fig. 1. The sulphur tube was placed close to the end of the discharge tube as in Fig. 2 and, at hydrogen pressures between 2 and 6 cm. Hg, an intense blackening of the lead acetate test-paper was obtained in about a minute. The applied potential was 10,000 volts (r.m.s.) at 400 cycles per second and the rate of flow was of the order of 10 litres per hour, measured at the pressure within the discharge tube. Much weaker colorations were obtained when the sulphur was placed at greater distances from the discharge tube. The gas from the discharge also turned yellow tungstic oxide greenish. These experiments demonstrated the formation of active hydrogen in considerable amount.

A quantitative investigation was therefore commenced in which the concentration of the sulphuretted hydrogen and, hence, of the active hydrogen producing it, was measured under varying conditions of formation. Fig. 2 shows the arrangement which was adopted for these experiments. The discharge tube has a gas space of width 0.14 cm. It was constructed of soft glass and the electrodes, which were water-cooled, were of mercury. The cooling tubes and electrodes were electrically connected according to the method described by Lunt.<sup>10</sup> The ozoniser constitutes a system of two condensers,  $C_1$  and  $C_2$ , which are connected in series.<sup>11</sup>  $C_1$  represents the capacity associated with the glass walls of the vessel and  $C_2$  that associated with the gas space.  $R$  represents the resistance of the gas space; its value will vary with the degree of ionisation.

The values of  $C_1$  and  $C_2$  were obtained by measuring<sup>12</sup> the capacity of the system when the gas space contained air and also when it was filled with mercury. The values are  $C_1 = 337$  and  $C_2 = 60.1$  micro micro farads.

Before commencing an experiment the tap D, Fig. 2, was opened and the glass spiral,  $L_1$ , was connected to the apparatus by turning B and C to the positions shown. The portion of the apparatus between the palladium tube and the oil pump (Hyvac) was then evacuated as completely as possible and the pump was maintained in action throughout the course of the experiment. The palladium tube, which served to regulate the rate of admission of hydrogen into the apparatus, was gradually heated until the desired rate of flow was attained, as indicated by the flowmeter, F. This flowmeter gave a deflection of 1 cm. Hg for a rate of flow of 0.363 litres per hour. The pressure was shown by the mercury manometer, M. When conditions were steady preliminary adjustments of voltage and frequency were made, and coils  $L_1$  and  $L_2$  were immersed in liquid air. Coil  $L_1$  served to remove mercury vapour from the gas before it entered the discharge tube, while coil  $L_2$  served to collect the hydrogen sulphide formed by the action of active hydrogen on the sulphur (Fig. 2). The discharge was then started and continued during an accurately timed interval of



<sup>10</sup> *Phil. Mag.*, 1926, 4, [ii]; 314.

<sup>11</sup> Warburg, *Ann. Physik*, 1909, 28, 1-17.

<sup>12</sup> An accurate bridge method was used. The author is indebted to Mr. M. A. G. Rau for these measurements.

5 mins. to 1 hr. according to the yield of sulphuretted hydrogen expected. During this period the pressure, rate of flow and electrical conditions were readily maintained constant within the limits of accuracy of the measuring instruments. After stopping the discharge the flow of hydrogen was continued for a period of five minutes.

Taps B and C were then turned so as to disconnect  $L_2$  from the remainder of the apparatus. The liquid air was removed and the hydrogen sulphide which had condensed in  $L_2$  was blown over, in a current of cylinder hydrogen, into the bubbler S. The bubbler contained 25 c.c. of centinormal iodine solution, which was afterwards back-titrated with a standard solution of arsenious oxide. Usually the amount of hydrogen sulphide absorbed was equivalent to 3 or 4 c.c. of the arsenic solution. The titration was accurate within  $\pm 0.05$  c.c. so that the errors involved in this method did not, in most cases, amount to more than  $\pm 2$  per cent.

*Variation of Yield of Active Hydrogen with Rate of Flow of Gas.*—These experiments were carried out at a pressure of 4 cm. Hg, and at

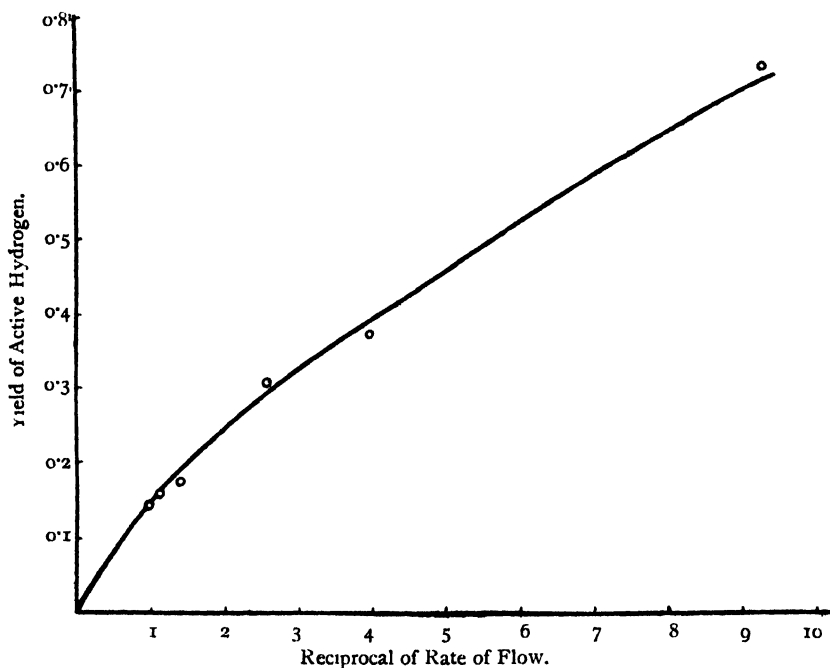


FIG. 3.

9000 volts (400 cycles per second). Table I. relates the yield of active hydrogen, expressed in milligrams per litre of gas measured at 76 cm. and  $16.5^{\circ}$  C., with the rate of flow of the gas expressed in litres per hour measured under the same conditions. In Fig. 3 is given the corresponding curve in which the yield is plotted against the reciprocal of the rate of flow, which is proportional to the reaction time or time for which the gas is exposed to the discharge. It is clear that, under the conditions of these experiments in which the sulphur was very close to the end of the discharge tube, the formation of active hydrogen increases with the time of exposure of any given volume of gas to the discharge. This increase must more than compensate for any increased decomposition of the activated gas during the

TABLE I.

9000 VOLTS R.M.S. AT 400 CYCLES PER SECOND; PRESSURE, 4 CM. HG.

Rate of Flow.	Yield of Active Hydrogen.	$\frac{w}{k}$
1.020 litres/hr.	0.143 mg./litre	1.09
0.904     "	0.159     "	1.09
0.714     "	0.175     "	0.99
0.392     "	0.308     "	1.01
0.254     "	0.374     "	1.09
0.109     "	0.735     "	1.25

time taken to traverse the very short distance between the discharge tube and the sulphur.

The curve shown is very similar in type to those obtained by Becker<sup>13</sup> relating to ozone formation in the silent electric discharge. Becker found that these curves might be represented by the following empirical equation—

$$C = \frac{w}{k + e_0 v} = \frac{w}{k} \cdot \frac{1}{1 + \frac{e_0}{k} v}$$

where  $C$  is the concentration of ozone and  $v$  is the rate of flow of the gas  $w$ ,  $k$  and  $e_0$  are constants. The values of  $\frac{w}{k}$  which are given in column 3 of Table I. are a result of an attempt to apply this equation to the data relating to active hydrogen formation. Nearly constant values of  $\frac{w}{k}$  are obtained

by putting  $\frac{e_0}{k} = 6.48$ . The mean of these values is 1.15, and the above equation shows that this represents the "Limiting Concentration"; i.e., the yield of active hydrogen corresponding to zero rate of flow.

*Variation of Yield with Voltage at Different Pressures.*—The data relating the formation of active hydrogen to the voltage applied to the ionisation vessel and to the gas pressure are given in Table II. In these experiments the high voltage line was fed from a transformer with a closed iron circuit, as is the case with all previous and subsequent experiments except where otherwise recorded. It was impossible to operate above 10,000 volts owing to the excessive sparking which took place across the glass surface of the discharge tube at voltages above this value. The corrected values of the yield given in column 5 of this table were obtained in the following way: It has been assumed that the percentage variation of the yield of active hydrogen with the rate of flow is independent of the pressure. On this hypothesis the data cited in Table I. have been utilised to reduce the data of column 4, Table II., to correspond with an arbitrarily chosen rate of flow of 19.38 litres per hour, measured at the pressure of the experiment. All the curves were drawn from the data after this correction had been applied.

The results of the watt measurements are given in column 2, of Table II. They show, within the limits of accuracy of the measurements, that the power developed in the gas is independent of the pressure over the

<sup>13</sup> *Wiss Veröff. Siemens-Konzern*, 1920, 76.

TABLE II.  
400 CYCLES PER SECOND.

Volts.	Watts.	Rate of Flow.	Yield of Active Hydrogen.	
			Uncorrected.	Corrected.
(a) Pressure, 1 cm. Hg.				
3950	3.0	0.185 litres/hr.	0.056 mg./litre	0.040
4800	4.6	0.160 "	0.184 "	0.136
5700	6.6	0.167 "	0.396 "	0.227
6600	8.4	0.167 "	0.673 "	0.387
7450	10.3	0.167 "	1.066 "	0.584
7870	11.2	0.163 "	1.605 "	0.979
9700	15.0	0.163 "	2.502 "	1.723
(b) Pressure, 2 cm. Hg.				
4800	4.6	0.370 litres/hr.	0.038 mg./litre	0.020
5700	6.6	0.370 "	0.116 "	0.085
6550	8.4	0.348 "	0.271 "	0.174
7450	10.3	0.344 "	0.546 "	0.342
8400	12.2	0.363 "	0.770 "	0.581
9450	14.4	0.359 "	1.281 "	0.910
(c) Pressure, 3 cm. Hg.				
6150	7.5	0.689 litres/hr.	0.028 mg./litre	0.022
6550	8.4	0.714 "	0.037 "	0.031
7650	10.7	0.740 "	0.142 "	0.130
8080	11.5	0.776 "	0.262 "	0.272
9200	13.9	0.852 "	0.354 "	0.469
9900	15.5	0.852 "	0.441 "	0.569
(d) Pressure, 4 cm. Hg.				
7000	9.3	1.020 litres/hr.	0.006 mg./litre	0.006
8100	11.6	1.020 "	0.062 "	0.062
9000	13.5	1.020 "	0.143 "	0.143
9450	14.5	1.020 "	0.171 "	0.171
9900	15.6	1.020 "	0.259 "	0.259
(e) Pressure, 5 cm. Hg.				
7450	10.3	1.486 litres/hr.	0.004 mg./litre	0.006
8300	12.0	1.468 "	0.019 "	0.028
9200	13.9	1.374 "	0.048 "	0.060

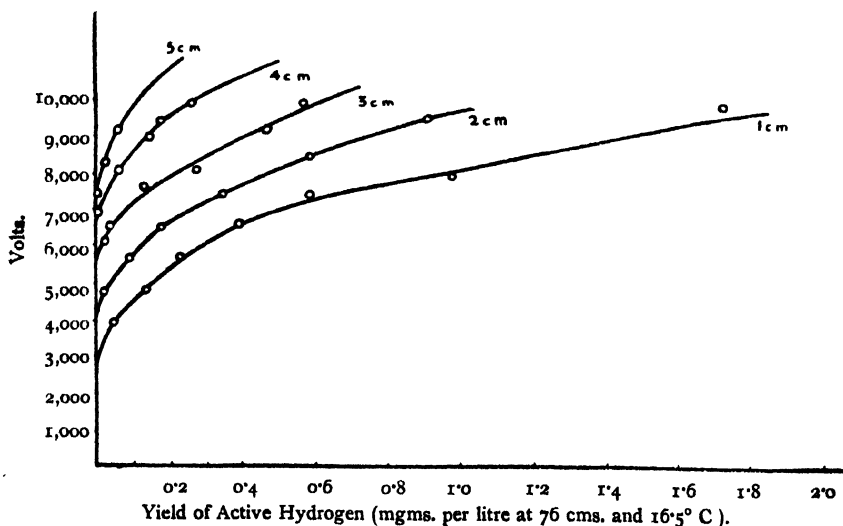


FIG. 4.

range from 1.5 cm. Hg. It was also found that the volts and watts are linearly related for potentials greater than 4 kilovolts.

The yield of active hydrogen, however, varies greatly with pressure and is not linearly related to the voltages, being practically zero above 6 or 7 cm. Hg, or below 3000 volts. In Fig. 4 the voltage is plotted against the yield of active hydrogen, while in Fig. 5 the data are treated in a different manner, the voltage being plotted against the pressure corresponding with a fixed value of the yield. A series of straight lines is thus obtained. It is of interest to plot the product of the logarithm of the yield,  $\log_{10} y$ , and the voltage,  $V$ , against the voltage, the curves so obtained are given in Fig. 6.

From the curves in Fig. 6 it is seen that the results for 1 cm. pressure and for 2 cm. pressure lie nearly on two parallel straight lines, while results for higher pressures are more erratic.

If it be assumed that the results of the above experiments, when due allowance has been made for unavoidable experimental error, are represented by a series of parallel and

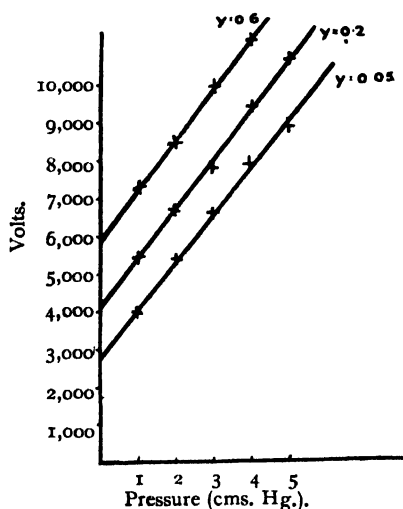


FIG. 5.

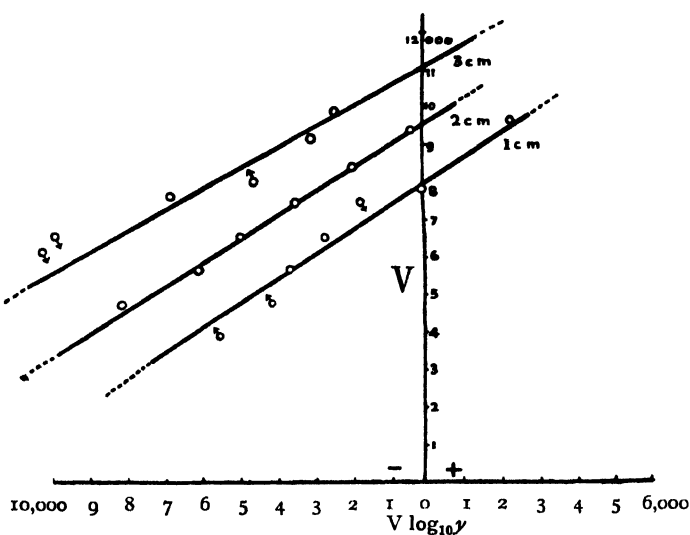


FIG. 6.

equally spaced straight lines, then the equations to the lines would be :

$$\text{Pressure} = 1 \text{ cm. Hg.} \quad V = 0.632 (V \log_{10} y) + 8000.$$

$$\text{Pressure} = 2 \text{ cm. Hg.} \quad V = 0.632 (V \log_{10} y) + 9600,$$

and so on.

Since the lines are equally spaced the variable parameter of this family of lines may be expressed as

$$A + Bp$$

where A and B are invariant.

From the above equations it follows that

$$A = 6400 \text{ and } B = 1600.$$

The general equation to the series of lines is therefore

$$V = 0.632 (V \log_{10} y) + 6400 + 1600p$$

which becomes

$$y = 38.2e^{-\frac{23320 + 5830p}{V}} \quad (1)$$

hence

$$\frac{23320 + 5830p}{V} = \log_e \frac{38.2}{y}.$$

From this last equation the slopes of the  $V$ - $p$  lines (Fig. 5) for different values of  $y$  may be calculated. Examples are given in Table III., where  $\theta$  is the angle between the lines and the axis of abscissæ.

It is seen that the lines in Fig. 5 are more nearly parallel than is indicated by the equation (1) above.

TABLE III.

$y$ .	Tan $\theta$ .	
	(From Curves.)	(Calculated.)
0.05	1.26	1.28
0.2	1.30	1.37
0.6	1.33	1.85

The equation therefore cannot be regarded as an exact representation of the results of Table II. and deviations of the points from the lines in Fig. 6 may not be due entirely to experimental error. Nevertheless equation (1) may be considered a nearly correct and a useful summary of the experimental results.

In the previous paper (p. 58) it is shown that the velocity of a chemical reaction produced in the silent electric discharge is given by

$$K = k \cdot p \cdot Nv \cdot e^{-V_0/lE} \quad (2)$$

where  $K$  is the initial velocity of the reaction,  $E$  the voltage gradient in the gas,  $l$  the mean free path of the ions and  $k$ , is a constant.

In this equation also,  $V_0$  (volts) represents the critical energy which an ion must possess in order that on collision of the ion with a molecule of the gas the latter may be activated or chemically changed;  $N$  is the number of pairs of ions per c.c. of gas and  $v$  is their average velocity.  $2Nv$  therefore represents the current carried by the ions.

Now,  $y$ , the yield of active hydrogen, is proportional to the number of molecules of active hydrogen formed per c.c. of gas while it is subjected to the discharge, divided by the total number of molecules per c.c. It would

appear therefore that in order to apply equation (2) to the present experiments, it is only necessary to write  $y \propto \frac{K}{p}$ . This gives

$$y = c \cdot Nv \cdot e^{-\frac{V_0}{E}} \quad (3)$$

It has been found that the ozoniser currents do not vary greatly with pressure over the range of pressures from 1.4 cm. Hg,  $Nv$  is therefore approximately independent of pressure and the conditions for the identity of equations (1) and (3) become

$$\frac{V_0}{E} = \frac{5830p}{V} \quad (a)$$

$$\text{and} \quad Nv \propto e^{-\frac{23320}{V}} \quad (b)$$

From (a) we may calculate  $V_0$  in terms of  $E$ . Now  $E = Vg/0.14$ , where  $Vg$  is the voltage across the gas space of width 0.14 cm. In order to evaluate  $Vg$  in terms of  $V$ , the applied voltage, the following procedure was adopted:—

The equivalent frequency of the A.C. supply at 400 cycles per second (nominal value determined from the speed of rotation of the generator), was calculated from measurements of the current through a condenser of known capacity, *viz.*:  $500\mu\text{F}$ . The value of the equivalent frequency was 411 cycles per second and was independent of the voltage. Ozoniser currents were measured with a moving-iron milliammeter reading from 0.50 milliamps. The currents did not vary with pressure by more than 5 per cent., over the range from 1.5 cm. Hg. Table III.a relates the applied voltage with the ozoniser currents (mean values) and the power developed in the gas. In column 5 are given the values of  $\cos \phi$ , the power factor, which was calculated in the usual manner.

TABLE III.a.

1.	2.	3.	4.	5.
Volts (Applied).	Ozoniser Currents.	$1 \times 2.$	Watts.	$\cos \phi.$
6000	$5.1 \times 10^{-3}$ amps.	30.6	7.2	0.24
7000	5.9    "    "	41.3	9.3	0.23
8000	6.6    "    "	52.8	11.4	0.22
9000	7.5    "    "	67.5	13.5	0.20

From a knowledge of the ozoniser currents and of the equivalent frequency, the voltage difference associated with the glass walls, of capacity  $337\mu\text{F}$ , could be calculated.  $Vg$ , the voltage drop across the gas space, was then obtained graphically by means of a vector diagram in the customary manner. Thus, for example, when  $V = 6000$ ,  $Vg = 1450$ , and when  $V = 9000$ ,  $Vg = 1800$  volt., approximately.

$V_0$  may be estimated from equation (a) with sufficient accuracy by writing  $V = 4.5 Vg$ .

Since

$$l = 1.125 \times 10^{-5} \times 76/p \text{ cm.}$$

we have

$$V_0 = 7.9 \text{ volts.}$$

The value of  $l$  used is that given by Jeans ("Dynamic Theory of Gases," p. 10) for the hydrogen molecule. If the ions effective in producing active hydrogen were electrons, the corresponding value of  $V_0$  would be  $4\sqrt{2} \times 7.9$  volts, since the mean free path of a high-speed electron is  $4\sqrt{2}$  times that of a molecule.<sup>14</sup> It would seem more probable, however, that positive and negative ions with the same kinetic energy are equally effective for the production of active hydrogen. On this hypothesis, since the two kinds of ions are present in equal numbers, the mean of the mean free paths for the positive and negative ions may be used to estimate  $V_0$ . In this way the value  $V_0 = 26.3$  volts is obtained.

In this connection it is interesting to note that Smyth,<sup>15</sup> as a result of a study of the ionisation potentials of hydrogen, has concluded that a potential of 16 volts is necessary for the ionisation of the hydrogen molecule and that, at voltages equal to or greater than 20.2 volts, some dissociation of the molecule probably occurs.

*Variation of Yield with Frequency.*—A transformer with open iron circuit was used for these experiments in order to reduce harmonics to a minimum. They were carried out at a constant voltage and pressure of 9000 volts and 2 cm. Hg, respectively. The results are given in Table IV.; they show that while the power developed in the gas is approximately proportional to the frequency, the yield of active hydrogen is not linearly related to either of these factors. The rate of increase of yield with frequency, or watts, is considerably greater in the range below 240 cycles per second than for frequencies above that value.

TABLE IV.

9,000 VOLTS R.M.S.      2 CM. Hg.      Transformer with open iron circuit.

1.	2.	3.	4.
Frequency.	Watts.	Rate of Flow.	Yield of Active Hydrogen (Uncorrected).
85 cycles per sec.	3.2	0.442 litres/hr.	0.089 mg./litre
145 " "	5.6	" "	0.177 "
213 " "	8.0	" "	0.310 "
278 " "	10.2	" "	0.352 "
332 " "	12.2	" "	0.372 "
540 " "	19.4	" "	0.420 "

*The Properties and Life Period of Active Hydrogen.*—It has been established that the active hydrogen which has been obtained is not appreciably destroyed by passage through a short plug of glass-wool. It is completely condensed in liquid air, but retains only about one-twentieth of its original activity after re-evaporation. A fine tungsten wire placed in the stream of active gas was not appreciably heated.

Experiments have been carried out which indicate the approximate life period of the active hydrogen. Data are given in Table V. which relate the yield of active hydrogen to the volume between the lower end of the discharge tube and the upper layer of sulphur. The figures in column 2 were calculated from the rate of flow of the gas (in this case 5 c.c. per second). It will be seen that most of the activity is lost in about 1/5th of

<sup>14</sup> Townsend, "Electricity in Gases," pp. 157, 293, Oxford, 1915.

<sup>15</sup> *Proc. Roy. Soc.* (1924), 105A, 116.

a second. The figures in column 1 were estimated roughly from the dimensions of the glass-tubing used; also no doubt some error was introduced owing to the presence of a small pellet of glass-wool which was placed on the upper surface of the sulphur, which served to hold it in position.

Nevertheless these experiments suffice to show the very short life period of the active hydrogen. In this connection it may be noted that Bonhoeffer

TABLE V.

Volume between Discharge Tube and Sulphur.	Time to pass from Discharge Tube to Sulphur.	Relative amount of Sulphuretted Hydrogen obtained.
0.5 c.c.	0.1 sec.	17.2
0.7 "	0.14 "	0.7
1.0 "	0.2 "	0.1
4.5 "	0.9 "	trace

obtained the value  $\frac{1}{2}$  sec. for the half-life period of monatomic hydrogen.

One further point of interest concerns the nature of the reaction between sulphur and active hydrogen. On examining the sulphur tube and adjacent tubing after long continued use, a deposit of finely-divided whitish sulphur could be seen just below the upper layers of crystalline sulphur. Traces of a similar white substance were also seen further along the tubing and especially at the point where the tubing, after leaving the discharge tube, first dips into the liquid air bath. This would appear to indicate that the action of active hydrogen on sulphur at ordinary temperatures results in the formation of an unstable and volatile polysulphide of hydrogen.

In conclusion, the author desires to express his thanks to the Ramsay Memorial Fellowship Trustees for a Fellowship, to Dr. R. W. Lunt for much valuable assistance at various stages in the development of this research and, also, to Professor F. G. Donnan, F.R.S., for his interest and instructive advice during its progress.

*University College, London.*

**Dr. H. Borns** inquired whether Mr. Elliott had also tried the arc method of Langmuir and experimented with Langmuir's flames of atomic hydrogen. Langmuir seemed to consider that the activation was essentially thermal and set in about 1300° C.

**Mr. W. Taylor** asked whether the theory of activation by ionic impact would not have to face the same problems as had been encountered by the theory of activation by molecular collisions. For example, in applying the general equation (6), the quantity  $K$  was really the rate of formation of activated molecules, which could be considered as an intermediate product in any chemical action taking place. The observed rate of appearance of end-products would depend upon the nature of the subsequent proceedings in which the activated molecules were involved, and might well involve a further collision frequency, and therefore another power of  $p$ . In addition, there was the loss of activated molecules due to reversion to the normal state.

**Professor Allmand** asked Dr. Lunt whether any work had been done on more complex reactions in which the critical activation energy might be regarded as being shared between two molecules before collision. In such

a case, the fundamental equation  $x_e = V_0 E^{-1}$  would presumably not hold. With regard to Mr. Elliott's paper, it was of interest that the life of the activated hydrogen appeared to be of the same order as that of Bornhoeffer's atomic hydrogen. He suggested that the results of an investigation of the activation of chlorine in the electric discharge would be of considerable interest to the photochemist, as the temporary formation of  $\text{Cl}_2$  molecules was now being assumed by several workers in discussing the kinetics of the hydrogen-chlorine reaction.

**Dr. E. G. Willey** (*contributed*): It is noticeable that both in Mr. Elliott's work and also in the earlier experiments of Wendt and Landauer very small yields of active hydrogen have been obtained, these never exceeding 0.01 per cent. by volume when the corona or ozoniser is employed. During the course of some recent work by the writer and Dr. E. K. Rideal upon active nitrogen a few experiments were performed with active hydrogen prepared by means of the condensed discharge as used in the production of the nitrogen afterglow, and here hydrogen sulphide was obtained equivalent to 0.5 per cent. active hydrogen and at least 0.7 second after the hydrogen had left the discharge. A similar result was obtained when the extent of activation was measured by admitting nitrogen downstream from the discharge, ammonia being formed. It is curious that when this stream of nitrogen was activated also no perceptible yield of  $\text{NH}_3$  was obtained, all other conditions being the same and so it appears probable that the ammonia first formed was under these conditions of experiment decomposed by the active nitrogen present.

The frequency of the discharge appears also to be of fundamental importance in the production of active nitrogen; the yield of this from a given discharge tube can often greatly be increased by the addition of a condenser of suitable capacity which is connected across the electrodes and appears to "tune" the circuit, so to speak. It would be of much interest if Mr. Elliott could extend his researches still further to a correlation of frequency, wave form and the production of active hydrogen, and the circumstances relative to its formation in the H.T. disruptive discharge.

**Professor Donnan**, in reply to the remarks of Mr. Taylor, pointed out that the theory given in the paper was a first attempt to analyse the mechanism of chemical reactions in the "silent" discharge. It was assumed that any molecule which received a critical energy increment by collision with an electron or ion of sufficient velocity became chemically active. It was of course, quite possible that a proportion of these active molecules might afterwards become de-activated by collision or by radiation. In its present form, the theory of chemical activation by ionic or electronic collision was stated in the simplest terms, and would doubtless require extension and elaboration. It had already led to a relationship which agreed in form with that obtained by Mr. Elliott from his results on the activation of hydrogen.

**Mr. Elliott** said that the active hydrogen obtained differed from the monatomic hydrogen of Langmuir, Wood and Bornhoeffer in its behaviour in contact with glass wool and tungsten, and at the temperature of liquid air. It thus resembled the 'hyzone' studied qualitatively by Wendt and others, although Wendt worked with much smaller concentrations than those obtaining in the experiments just described, in which the greatest amounts of active hydrogen observed were of the order of 1 per cent. by weight. Probably in both cases the active hydrogen consisted of aggregates each comprising one hydrogen atom linked to one or more hydrogen molecules; recombination of the active hydrogen to form ordinary hydrogen might therefore be expected to be bimolecular and largely dependent on the

concentration of the active form. A study of the influence of both wave form and frequency on the production of chemical change in the silent electric discharge was certainly desirable, and they hoped to carry out experiments of this nature very soon.

**Dr. Lunt** explained that the expression for the velocity constant of a reaction, in which chemical change is caused solely by collisions between reactant molecules and ions, was obtained on the assumption that every encounter in which the ion possesses energy equal to, or greater than,  $V_0e$ , results in the formation of a chemically changed and stable molecule. No attempt had yet been made to derive an equation for more complex types of reaction. The fact that linear relationships, in the form of equation (5), leading to definite values of  $V_0$  had been obtained in the case of active hydrogen, and in the decomposition of nitrous oxide (to be published shortly by Mr. Joshi) was thought to warrant the presentation of the theory in this simple form.

It would be interesting to know if Dr. Willey has measured the current and frequency in his condensed discharge experiments. It is difficult to see in what way a condenser connected across the electrodes could be said to tune the circuit, for any such circuit has a characteristic natural frequency; without a knowledge of the circuit constants it is impossible to predict what influence the condenser would have on this frequency. Generally, it would have the effect of increasing the current across the electrodes, and this current is undoubtedly an important factor in the production of chemical change by an electric discharge.

## THE SORET EFFECT. PART I.

BY C. C. TANNER.

(Communicated by PROFESSOR F. G. DONNAN, C.B.E., F.R.S.)

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When a temperature gradient exists in a solution, then, in general, a concentration gradient is set up. Several workers<sup>1</sup> have attempted to measure the *Soret Equilibrium* concentration gradient in aqueous solutions, principally of electrolytes.

The means employed have invariably required a considerable time for the establishment of the limiting concentration gradient.

The present work was commenced with the object of measuring the effect in mixtures of organic liquids. After some preliminary experiments, carried out by older methods, attention was concentrated on the elaboration of a method in which the establishment of the limiting concentration gradient was rapid. An optical method of measuring the concentration changes in presence of the temperature gradient was devised and has been used to measure the effect in aqueous solutions of electrolytes. The study of the effect in those solutions presented many points of interest; it was

<sup>1</sup>Ludwig, *Wien. Akad. Ber.* (1856), 20, 539. Soret, *Arch. de Genève* (1879), 3, 48; (1880), 4, 209; *Ann. Chim. et Physique* (1881) (5), 23, 293. Berchem, *Compt. rend.* (1890), 110, 82. Abegg, *Z. physikal. Chem.* (1898), 26, 161. Arrhenius, *Z. physikal. Chem.* (1898), 26, 187. Scarpa, *Atti. R. Accad. Lincei* (1908), 17, 362. Wereide, *Ann. Physique* (1914) (9), 2, 67. Chipman, *J. Amer. Chem. Soc.* (1926), 48, 2577.

facilitated by the relatively fast rates of diffusion of electrolytes and the low temperature coefficient of refractive index of their aqueous solutions, and afforded a means whereby the results of the method could be checked against those of previous workers.

In this paper the method is described and the results obtained in the case of aqueous solutions are summarised.

A good method should satisfy the following conditions:—

- (1) Diffusion to be rapid, so that  $t_{\infty}$ , the time required for the establishment of the steady state, is not longer than 24 hours.
- (2) Measurement of concentration changes to be effected without disturbing the solution in any way.
- (3) Method to be applicable to mixtures of organic liquids.
- (4) Method to be available over a wide concentration range.

The first requirement necessitates a diffusion column of small vertical dimensions—the height must not be greater than 10 mm. Owing to this restriction and to conditions (2) and (3) only optical methods of analysis can be used.

The cell in which the solution is placed must consist of an upper, heating plate and a lower, cooling plate with intervening walls of non-heat-conducting material transparent in the path of the beam. To ensure a uniform temperature gradient and to minimise convection errors at the walls of the cell, the cell length must be great compared with its height.

### Optical Analysis of the System in Presence of the Temperature Gradient.

The optical methods developed by Wiener, Heimbrodt, Thovert and Clack<sup>2</sup> give a value of  $\frac{d\mu}{dx}$ , the rate of change of the refractive index,  $\mu$ , with the height of the cell,  $x$ , at a given height, say  $x_r$  in the cell.

Let  $\mu_1$  and  $\mu_2$  be the refractive indexes of the extreme layers in the cell corresponding with the temperatures  $T_1$  and  $T_2$  at a given time. The refractive index difference  $\mu_2 - \mu_1$  may be due in part to the temperature coefficient of refractive index of the solution, in part to a concentration change.

Then

$$\begin{aligned}\Delta\mu &= \mu_2 - \mu_1, \\ &= \int_1^2 \frac{d\mu}{dx} \cdot dx,\end{aligned}$$

and can be evaluated if  $\frac{d\mu}{dx}$  is known as a function of  $x$ , i.e., if  $\frac{d\mu}{dx}$  is known for the elementary horizontal layers in the cell.

It has been shown by Wiener that the small deviation,  $\alpha$  radians, of a beam of parallel, monochromatic light incident horizontally on a medium at a height  $x_r$  and passing through a length  $l$ , is numerically equal to the product of the length and the rate of change of the refractive index with  $x$  at the height  $x_r$ , i.e.,

$$\alpha = l \left( \frac{d\mu}{dx} \right)_{x = x_r}$$

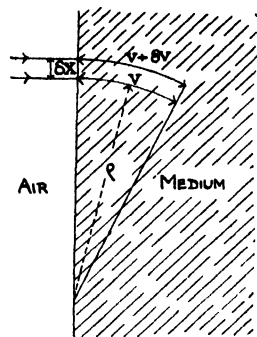
This equation is derived in the following way: Consider the incidence

<sup>2</sup> Wiener, *Wien. Ann.* (1893), **49**, 105. Thovert, *Ann. Chim. et Physique* (1902), **26**, 366. Heimbrodt, *Drudes Ann.* (1904), **13**. Thovert, *Ann. Chim. et Physique* (1914) (9) **2**, 369. Clack, *Proc. Physical Soc.* (1924), **36**, 313.

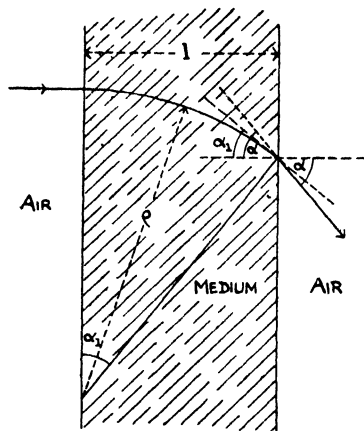
of a horizontal, parallel beam of monochromatic light on a medium in which the refractive index diminishes with the height but remains constant over any horizontal plane:—

From two secondary centres of disturbance in the wave front, separated by a distance  $\delta x$ , waves will spread into the medium with velocities  $v$  and  $v + \delta v$ , where  $\delta v$  is the change in the velocity of the light in the medium corresponding with a change in height  $\delta x$ . It is clear that the beam will be deviated towards the optically denser layers. If  $\rho$  be the instantaneous radius of curvature of the deviated beam,

$$\begin{aligned} \frac{\rho}{\rho + \delta x} &= \frac{v}{v + \delta v} \\ \therefore \frac{1}{\rho} &= \frac{1}{v} \cdot \frac{\delta v}{\delta x} \\ &= \frac{1}{\mu} \frac{d\mu}{dx}, \text{ numerically,} \end{aligned} \quad (1)$$



Consider the passage of the beam, here denoted by a single line, through an optical cell of the medium of length  $l$ . The angles in the figure are much exaggerated:—



In practice the angles  $\alpha$  and  $\alpha_1$  are arranged to be small ( $0.04$  radian at most). Hence we can write

$$\alpha = \mu \alpha_1 \quad (2)$$

$$\alpha_1 = \frac{l}{\rho} \quad (3)$$

Multiplying 1, 2 and 3,

$$\alpha = l \frac{d\mu}{dx}$$

In the following method of Thovert it is possible, by making a single movement of a camera shutter, to get an image on a photographic plate from which  $\frac{d\mu}{dx}$  at different heights can be calculated.

The incident beam of light is passed through a fine slit, inclined at an angle  $\theta$  to the horizontal in a plane perpendicular to the beam, before passing through the cell. In this way the small elements of the light projected from the slit pass through the cell at different heights and the deviations they experience are a measure of  $\frac{d\mu}{dx}$  over those different horizontal layers of solution through which they pass. The system is shown diagrammatically in Fig. 1.

The emergent beam is focussed on the plate by the cylindrical lens, placed so that it has no power in a horizontal direction and set at infinity. If no deviation occurs in the cell the image on the plate is a central, horizontal line parallel with OZ; otherwise it is displaced and, in general, curved.

When the contents of the cell are in an isothermal condition no deviation is produced. The image of the undeviated beam on the plate will be referred to as the "isothermal" line and is an absolute line of reference for

vertical measurement. If  $\frac{d\mu}{dx}$  be not equal to zero in the cell and cell walls, each element of the projected, inclined beam will be deviated through an angle  $\alpha$ , depending on the length of medium traversed and the mean value of  $\frac{d\mu}{dx}$  over the path. Hence each corresponding element of the image on the plate will be displaced through a distance  $y$ , where

$$\frac{y}{f} = \alpha = l \frac{d\mu}{dx},$$

$f$  being the focal length of the camera lens.

It follows that

$$\frac{d\mu}{dx} = \frac{y}{lf}.$$

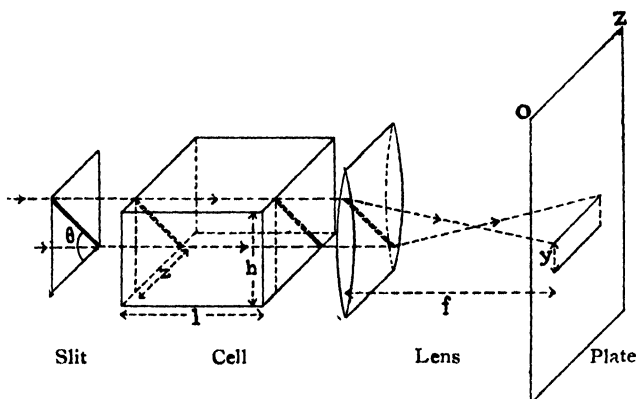


FIG. 1.

Hence the displacement  $y$  is proportional to the rate of change of the refractive index. If, as before,  $\mu_1$  and  $\mu_2$  are the refractive indexes of the extreme layers in the cell, the vertical height of which is  $h$ , then

$$\begin{aligned} \Delta\mu &= \mu_2 - \mu_1 = \int d\mu = \int_0^h \frac{d\mu}{dx} dx, \\ &= \bar{\frac{d\mu}{dx}} h. \end{aligned}$$

where  $\bar{\frac{d\mu}{dx}}$  is the mean value of the rate of change of the refractive index.

Therefore 
$$\Delta\mu = \frac{h}{lf} \bar{y}$$

where  $\bar{y}$  is the mean value of the displacement of the image.

Thus 
$$\Delta\mu = \frac{h}{lf} \cdot \frac{\sum ny}{n} \quad \dots \quad (4)$$

where  $n$  is the number of measurements made.

The determination of the refractive index difference rests on the measurement of the apparatus constants  $h$ ,  $l$  and  $f$  and the mean vertical displacement of the image from the "isothermal line."

*Test of Theory.*—A check on the accuracy of equation (4) is afforded

by an experiment in which a pure liquid of known temperature coefficient of refractive index is placed in the cell. The value of  $\frac{\Delta\mu}{\Delta T}$  obtained from equation (4) by dividing throughout by  $\Delta T$ , the temperature difference between the plates, is compared with  $\frac{d\mu}{dT}$  for the mean temperature obtained from tables.

Such a control experiment was made with pure water:—

On measuring up the plate,  $\frac{\Sigma 10y}{10} = 0.701$  cm.

Also  $\frac{h}{jf} = 0.002434$ ,

and  $\Delta T = 13.95^\circ \text{C.}$

Therefore, numerically,  $\frac{\Delta\mu}{\Delta T} = 0.000122$ .

But the negative sign is required since  $y$ , the displacement of the image, is measured downwards. So

$$\frac{\Delta\mu}{\Delta T} = -0.000122.$$

From the tables of Landolt and Bornstein,

$$\left(\frac{d\mu}{dT}\right)_{30.8} = 0.0001215.$$

In the calculation the deviation due to the glass of the cell walls has been neglected. From the cell dimensions and the value of  $\frac{d\mu}{dT}$  for glass the correction is about 1 per cent.

*Application to Measurement of Thermal Diffusion.*—When the solution in the cell is in an isothermal condition  $\frac{d\mu}{dx}$  is equal to zero; as the temperature gradient is established  $\frac{d\mu}{dx}$  rapidly arrives at a value determined by  $\frac{d\mu}{dT}$ , the temperature coefficient of refractive index of the solution and  $\frac{dT}{dx}$ , the temperature gradient in the cell and, as time proceeds,  $\frac{d\mu}{dx}$  still further changes, as a concentration gradient is built up. In the case of aqueous solutions of electrolytes the initial "temperature" refractive index gradient is found to steepen, if it changes at all.

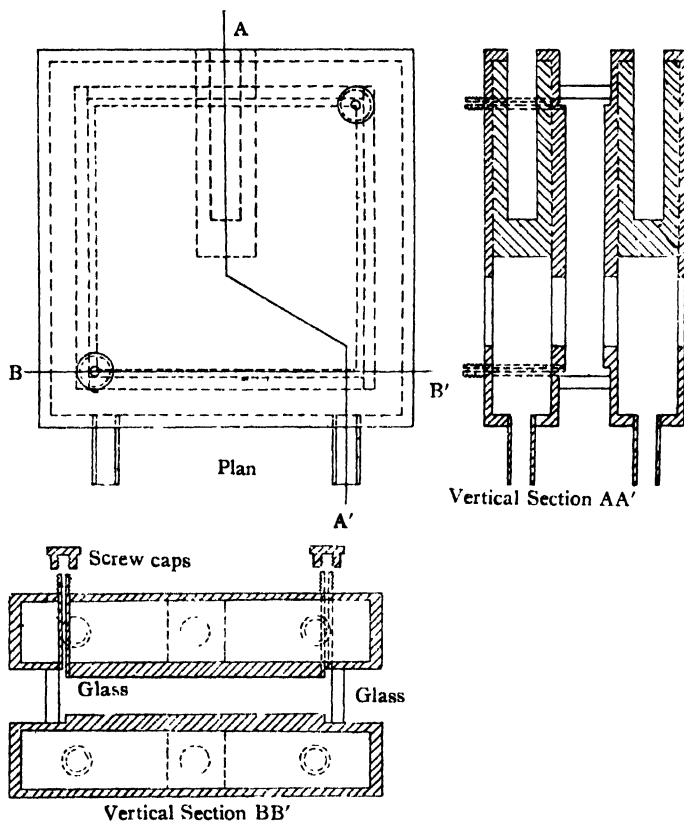
The value of the "temperature" change of refractive index can be measured by observing the displacement of the image as soon as possible after the commencement of the experiment, *i.e.*, as soon as there is a steady flow of heat through the cell.

The value of the combined "temperature" and solution effect can be found by measuring the limiting displacement as the time is prolonged.

It is essential that the time required for the establishment of the temperature gradient in the cell be small compared with the time required for the attainment of the limiting concentration gradient so that no appreciable concentration change takes place before the thermal conditions in the cell become steady.

**Description of Apparatus.**

*Cell.*—The cell is shown in Fig. 2. The solution is bounded top and bottom by the silver-plated surfaces of two hollow copper blocks through which water is passed at constant rate and, on the sides, by four glass strips. The glass strips in the path of the beam are optically plane. The glass and metal parts are assembled by means of a cement such as an insoluble wax fairly soft at  $100^{\circ}\text{C}$ . It is essential that the cement be not too brittle as in that case it invariably cracks when the temperature gradient is set up. The cell is firmly clamped in a reproducible position between two hard-wood heat-insulating blocks, the lower one of which is levelled



Diffusion Cell, Plan, and Sections (half size).

FIG. 2.

by means of three levelling screws and bolted in position. The solution is introduced by means of two narrow silver tubes passing vertically through the upper block and fitted with screw caps. A cell in which the copper blocks are faced with plates of solid silver is used in dealing with solutions such as those of concentrated acids or alkalies.

*Thermal Regulation and Measurement.*—The copper blocks are kept at constant temperature by the circulation of water from two electrically heated thermostats controlled by toluene-mercury regulators. The circulation is effected by means of two Rotoplunge pumps driven from the same motor.

The temperatures of the two copper blocks are read to  $1/20$  degree from two mercurial thermometers the bulbs of which are placed, with a trace of glycerine, in pockets drilled in the metal. The thermometers are calibrated by comparison with a standard thermometer furnished with N.P.L. Certificate.

*Optical Apparatus.*—Parallel light is obtained by means of the collimator of a spectroscope permanently fixed in a horizontal position. The slit is removed and in its place is substituted a piece of copper foil perforated with a minute opening of about  $.01$  cm. diameter. This approximately point source is flooded with light from a 500 candle power "Pointolite" lamp focussed by means of a small condensing lens. The slit takes the form of two razor-edges separated by a few tenths of a millimeter and permanently clamped in position.

The parallel light from the slit, after projection through the cell, is received by a fixed focus camera fitted with a cylindrical lens of focal length 50 cm. and aperture 2.5 cm. The slide is adapted to take small photographic plates  $1\frac{1}{8}$  inch by  $3\frac{1}{4}$ , four of which are cut from a single quarter plate.

Source of light, collimator, slit and cell are rigidly mounted on a baseboard as shown in Fig. 3 and screwed to a table placed in the least disturbed quarter of a room. The water from the thermostats, after passing through the pumps, is returned through rubber tubes to long glass spirals of short radius placed in the respective thermostats whence by short lead-tubes it passes through the apparatus and back to the thermostats. In this way pulsation in the water circulated is eliminated and the system protected from the disturbing effect of vibration.

*Adjustment of Apparatus.*—The object is to obtain a sharp shadow-image of the slit upon the plate. The collimator is adjusted until the issuing beam maintains a constant diameter for several yards: the light is then practically parallel. Collimator and camera are levelled with a spirit level and clamped permanently in position. The width of the slit is reduced to a minimum, namely a few tenths of a millimeter. Further reduction broadens the image and by cutting down the amount of light necessitates a long exposure. The point diaphragm of the collimator is reduced to about  $0.01$  cm. to obtain closely parallel light. A limit is set by

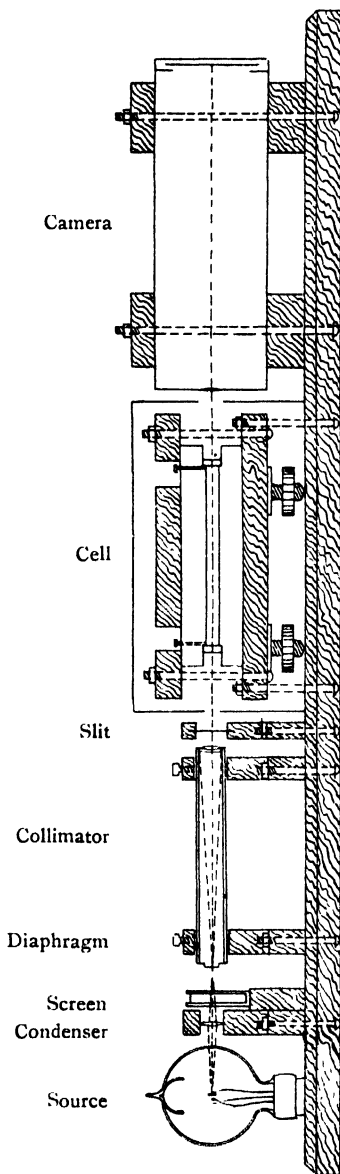


FIG. 3.

the consequent reduction of intensity. Further sharpening is effected by means of a light filter—a solution of Malachite Green in glycerine which passes light of F quality. The exposure required with Wellington Anti-screen plates is 20 seconds. Under the above conditions the lines on the plate can be measured to 0.002 cm. In order to make observations with highly-coloured liquids, such as the solutions of  $\text{CuSO}_4$ ,  $\text{NiSO}_4$ , and  $\text{CoSO}_4$ , in the cell the light filter is removed, since such solutions serve as their own screens, and exposures are taken, when necessary, on Ilford Panchromatic plates.

### Technique of Measurement.

*Solutions used.*—The well-defined crystalline chlorides and sulphates were weighed out and dissolved up to a known volume at room temperature. A check determination of the normality was made in the case of the chlorides by Volhard titration and in the case of the sulphates by gravimetric estimation as  $\text{BaSO}_4$ . The acids were standardised against crystalline calcite and provided solutions against which the solutions of KOH and NaOH were estimated by titration.

*Experimental.*—The cell was removed from its table and placed in an inclined position; the solution under test was introduced through the lower filling tube the displaced air escaping through the upper tube. The cell was replaced on its table; clamped in position and covered with a screen to cut off draughts and stray light. The thermometers were inserted. Water from the thermostat at the lower temperature  $T$  was circulated first through the upper, then through the lower block to bring the system to an isothermal condition. After ten minutes a trial exposure was made on a plate, which was immediately removed and developed. A central horizontal line on this plate indicated uniformity of temperature in the cell and was a sign that an experiment could be started. A second plate was inserted and a similar "isothermal" line was registered. The time was noted— $t = 0$ . The cover was removed; the water at  $T_1$  diverted from the upper block and that at  $T_2$  circulated in its place. At the end of five minutes the temperatures indicated by the thermometers had practically reached their final values. Temperatures and time were noted; the cell was closed by means of the screw caps and the cover replaced. Ten minutes after making the initial "isothermal" exposure a second exposure was made on the same plate and the temperatures noted. At intervals varying from five minutes to ten or twenty-four hours further exposures were made on the same plate, the temperatures and time being noted in each case. The plate was removed and developed and generally the experiment was then stopped. Occasionally, instead of stopping the experiment, a second plate was inserted, an exposure was immediately made and the temperature gradient in the cell was maintained overnight or over the week-end, when final exposures were made. In the case of slowly-diffusing substances, further changes in the position of the image on the plate were found, but in the case of rapidly-diffusing acid, alkali, and halide solutions the images obtained on the last plate practically coincided. The observations were recorded in the following way:—

*Experiment A.*2.035 N.  $\text{ZnSO}_4$ .

Time.	Temperature Cent.			Notes.
	Hot.	$\Delta T$ .	Cold.	
17/4/26 9.45 a.m.	23°07		22°90	" Isothermal " exposure made.
9.50 "	37°50		23°40	
9.55 "	37°77	14°17	23°60	Second exposure on same plate.
10.58 "	37°93	14°20	23°73	Third " " "
12.14 p.m.	38°00	14°20	23°80	Fourth " " "
1.30 "	38°05	14°25	23°80	Fifth " " "
3.15 "	38°05	14°25	23°80	Sixth " " "
3.17 "	38°10	14°27	23°83	First exposure on fresh plate.
11.30 "	38°00	14°15	23°85	Second " " "
18/4/26 10.30 a.m.	38°05	14°15	23°90	Third " " "
10.30 p.m.	38°10	14°11	23°99	Fourth " " "
19/4/26 8.14 a.m.	38°17	14°17	24°00	Fifth " " "

*Experiment B.*

3.99 N. KI.

Time.	Temperature Cent.			Notes.
	Hot.	$\Delta T$ .	Cold.	
9.53 a.m.	22°85		22°80	" Isothermal " exposure made.
9.58 "	37°80		23°10	
10.03 "	38°15	14°35	23°70	Second exposure on same plate.
10.13 "	38°15	14°30	23°75	Third " " "
10.28 "	38°10	14°30	23°80	Fourth " " "
10.43 "	38°05	14°30	23°75	Fifth " " "
10.58 "	38°00	14°25	23°75	Sixth " " "
11.30 "	38°05	14°35	23°70	Seventh " " "
12.21 p.m.	38°10	14°35	23°75	Eighth " " "
2.29 "	38°15	14°35	23°80	Ninth " " "
5.00 "	37°85	14°10	23°75	Tenth " " "

*Measurement of Plate.*—Note on the shape and meaning of the images.

The appearance of the plates obtained in the two representative experiments, selected to show the difference between slowly- and rapidly-diffusing solutions, is shown in Fig. 4. In each case the isothermal line is in the centre and the ends corresponding with the hot and cold layers are marked H and C. It will be observed that the first deviated lines are convex upwards; that the convexity diminishes in the succeeding lines and that the final ones are linear. An experiment made with pure water in the cell showed a first deviated line which was linear as indicated in Fig. 5. The convexity of

the deviated lines only appears with solutions in which diffusion takes place.

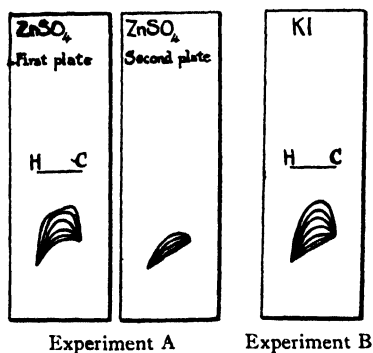


FIG. 4.

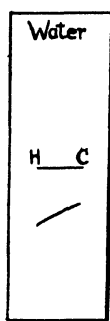


FIG. 5.

Since horizontal distances on the plate refer to vertical distances in the cell, it is clear from Fig. 4 that in the diffusing solutions an extremely rapid concentration change proceeds in those layers nearest the hot and cold plates, producing, during the early stages of the experiment, a steep local refractive index gradient in those layers. This local refractive index gradient approximates to the final, limiting refractive index gradient since the join of the extremities of the first deviated lines gives very closely the position of the final image, which is again linear. The change at the plates is much more localised in the case of the slowly-diffusing sulphate solutions and the figure shows that the first deviated line is practically linear in the centre and approximately parallel to the final deviated line.

Proof that the convexity of the lines does not indicate a non-uniform temperature gradient varying with the time is afforded by a glance at Fig. 5 illustrative of the plate obtained with pure water and also by the following comparison experiments:—

Exposures at minute intervals were taken immediately after the break-up of the isothermal system, first with a solution of KI then with pure water. The absence of any trace of convexity and the final linear character of the line on the plate obtained from the latter showed that the temperature gradient was regular, whilst the incipient appearance of bending at the extremities in the case of the former, even when the temperature gradient was being established, gave evidence of the rapidity of the diffusion process which was taking place at the plates. The curves obtained are shown in Fig. 6.

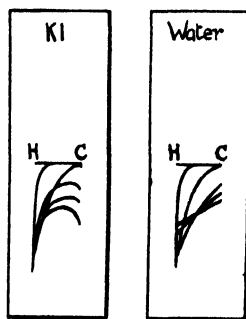


FIG. 6.

Owing to the presence of the base of the cell the light passing near the bottom, cold plate will be intercepted and will fail to register on the plate if there is any deviation. Hence, the extremities of the isothermal line, only can be referred to the extreme layers of liquid in the cell. Since only small angles of deviation are used, the curtailment of the displaced images, shown in Fig. 7, does not amount to 1/10th of the whole.

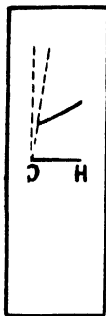


FIG. 7.



FIG. 8.

From the plate a mean value of the vertical displacement of the crest of each line from the isothermal line was measured. The transparent plate was pressed, film downwards, on a sheet of graph paper ruled in mm. squares placed on the table of a travelling microscope. The displacements of the curves from the isothermal line along "n" graph lines 1 mm. apart, as shown in Fig. 8, were measured and the mean taken. The number "n" might be 2, 3, 4, 5-10 according to the convexity of the lines. The mean of three settings of the

microscope wires was taken which could be reproduced to .002 cm. The measurements from a single plate were recorded in the manner shown in Table I. The temperature difference between the plates varied slightly in

the course of an experiment. The variation was small and the smooth curve drawn through the experimental points in the plot of the displacement from the isothermal line against the time could be referred to the mean temperature difference. Or a small correction could be applied, for the thermal displacement,  $y$ , was as a first approximation proportional to the temperature difference. Such a correction has been applied in Table I.

*Graphical Method for Obtaining the Effect due to Diffusion Alone as the Time is Prolonged.*—A plot of the corrected displacement of the crests of the deviated lines from the isothermal line against the time is shown in Fig. 9. The limiting displacement as the time is indefinitely increased

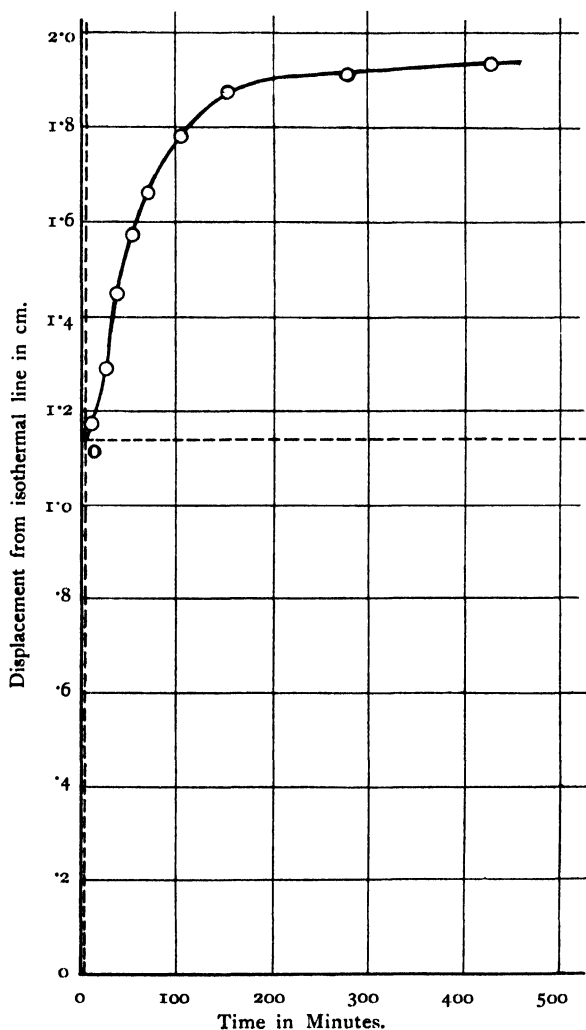


FIG. 9.

measures the sum of the refractive index changes due to the temperature-gradient and the concentration gradient which results from diffusion. It remains to separate the rapid temperature effect, practically complete in five minutes, from the combined effect. This is done graphically as follows :—

TABLE I.

Setting of Microscope Wires on										
"n."	Isothermal.	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.	9th Line.
	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.
1	7.061 57 58	8.236 39 39	8.350 53 48	8.517 19 19	8.631 28 26	8.720 18 19	8.831 35 32	8.933 35 32	8.971 78 71	8.971 78 71
2	7.064 60 53	8.240 42 40	8.351 51 49	8.508 09 10	8.627 23 24	8.713 12 12	8.835 30 37	8.934 37 36	8.978 80 79	8.978 80 79
3	7.061 61 60	8.232 52 52	8.370 74 71	8.522 23 24	8.637 35 38	8.725 24 24	8.848 49 49	8.942 42 42	8.991 92 91	8.991 92 91
1	7.059	8.238	8.351	8.518	8.628	8.719	8.833	8.931	8.973	8.973
2	7.062	8.241	8.350	8.509	8.625	8.712	8.836	8.936	8.979	8.979
3	7.061	8.232	8.374	8.523	8.637	8.724	8.849	8.942	8.991	8.991
	Displacement from Isothermal of	1st	2nd	3rd	4th	5th	6th	7th	8th	9th Line
1		1.179	1.202 - .007	1.459	1.569	1.660 + .003	1.774 - .003	1.872 - .003	1.914 - .003	1.914 + .014
2		1.179	1.288 - .007	1.447	1.563	1.650 + .003	1.774 - .003	1.874 - .003	1.917 - .003	1.917 + .014
3		1.191	1.313 - .007	1.462	1.576	1.663 + .003	1.788 - .003	1.881 - .003	1.930 - .003	1.930 + .014
$\Delta T$		14.55° C.	14.50° C.	14.40° C.	14.40° C.	14.35° C.	14.45° C.	14.45° C.	14.45° C.	14.20° C.
1		1.167	1.285	1.459	1.569	1.663	1.771	1.869	1.911	1.928
2		1.167	1.281	1.447	1.563	1.653	1.771	1.871	1.914	1.931
3		1.180	1.306	1.462	1.576	1.666	1.785	1.878	1.927	1.944
$\Delta T$		14.40° C.	14.40° C.	14.40° C.	14.40° C.	14.40° C.	14.40° C.	14.40° C.	14.40° C.	14.40° C.
	Sum:—	3.514	3.872	4.368	4.708	4.982	5.327	5.618	5.752	5.803
	Mean:—	1.171 cm.	1.291 cm.	1.456 cm.	1.570 cm.	1.661 cm.	1.776 cm.	1.873 cm.	1.917 cm.	1.934 cm.
	Time (minutes):—	10	20	35	50	65	97	148	276	423

The ordinate  $t = 5$  is drawn in and represents the Y axis for the isolated diffusion curve. The curve is next produced back to cut the new Y axis in O. Then the limiting displacement measured from O, the new zero, is a measure of the diffusion change alone. If  $y_0$  be the limiting displace-

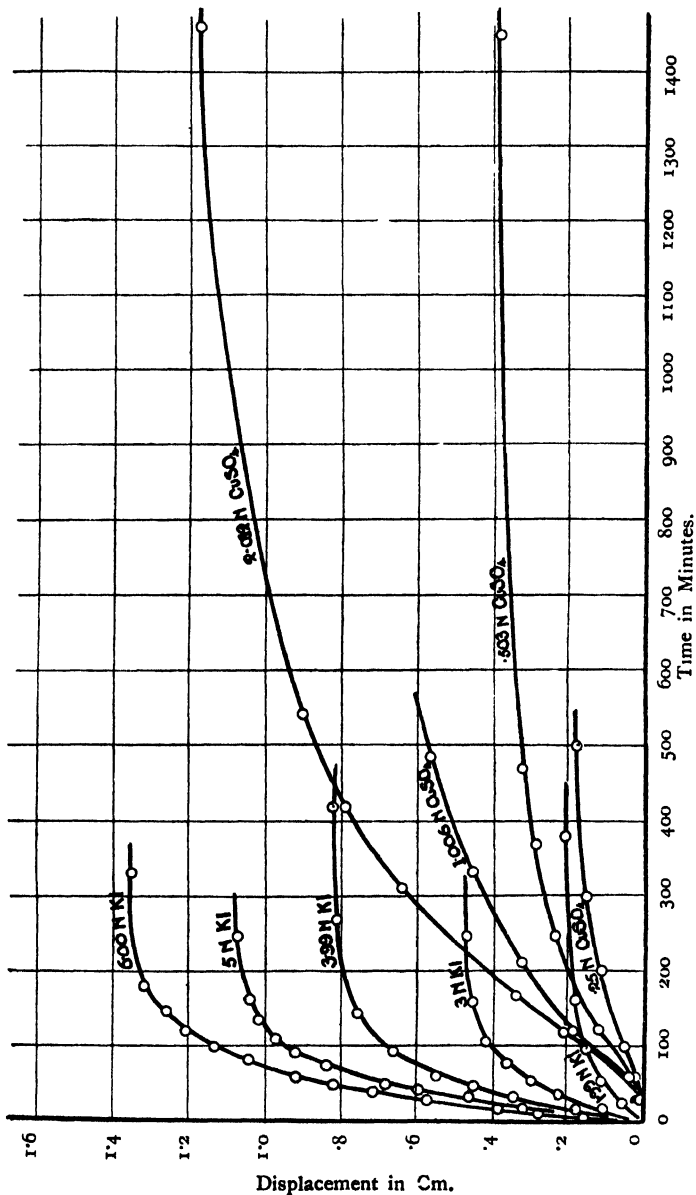


FIG. 10.

ment, then the refractive index difference, which measures the concentration difference alone, is given by

$$\Delta\mu = \frac{h}{f} y_0.$$

Representative isolated diffusion curves for solutions of KI and  $\text{CuSO}_4$  are shown in Fig. 10.

The direct method of obtaining  $y_0$ , the limiting diffusion displacement, is by graphical extrapolation of the curve to a large value of  $t$ . Instead of producing to  $t = \infty$ , it is more convenient to plot a function of the displacement against the reciprocal of the time and produce the curves back through a short distance to  $1/t = 0$ . The plot of  $\log_{10} y$  against  $1/t$  is found to be linear for sufficiently small values of  $1/t$  and has been used to determine  $\log_{10} y_0$ . In Fig. 11 the displacements are shown plotted on a logarithmic scale so that the limiting displacement  $y$  is given directly by the intersection of the curves with the OY axis.

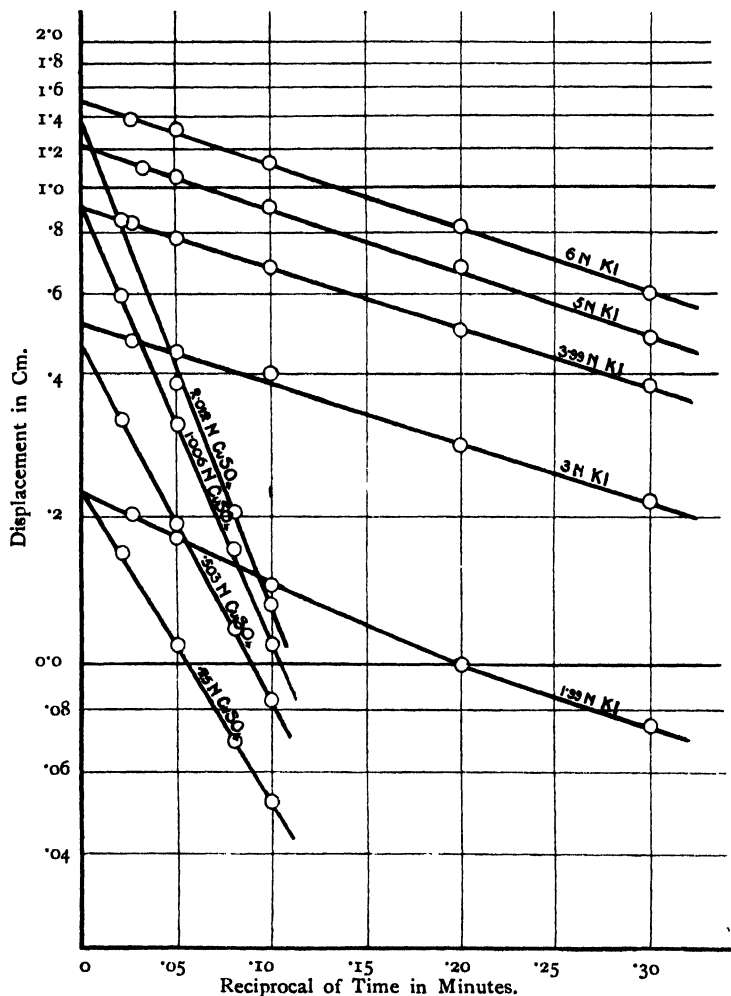


FIG. 11.

*Calculation of the Concentration Change  $\Delta N$  Corresponding with the Refractive Index Change  $\Delta \mu$ .*

We have 
$$\Delta \mu = \mu_2 - \mu_1 = \frac{h}{\lambda f} \cdot y_0.$$

Since  $y$  is negative, being measured downwards from the isothermal line,  $\Delta\mu$  is always negative. If this is borne in mind only the numerical values of the quantities in the expression need be considered.

- $|y_0|$  is obtained graphically;
- $h$  is the vertical height of the cell and is measured with the cathetometer;
- $l$  is the length of solution traversed by the beam and is measured with a steel rule;
- $f$  is the focal length of the camera lens and is measured with a metre stick.

The expression  $h/lf$  can also be obtained by a calibration experiment with pure water when

- $y$  is measured on the plate;
- $\Delta\mu$  is calculated from the known temperature coefficient of water (at the mean temperature) and the temperature difference between the plates.

In order to convert  $\Delta\mu$  to  $\Delta N$  a value of the rate of change of the refractive index of the solution with the concentration is required for the particular concentration of the solution under test. This rate of change varies slightly with the temperature, but its value for the mean temperature of the solution in the cell can be used without introducing much error. The refractive indexes of the solutions used were determined with a Hilger Pulfrich Refractometer. The relation between refractive index and concentration of the solution can be taken as

$$\mu = a + \beta N + \gamma N^2$$

where  $\mu$  is the refractive index;

$N$  is the concentration expressed in gm. equivs./litre.

$a$  is clearly the refractive index of pure water,  $\mu_0$ .

Therefore

$$\mu - \mu_0 = \beta N + \gamma N^2.$$

And  $\beta$  and  $\gamma$  can be calculated by measuring the refractive index of two solutions of known concentration. Hence  $\frac{d\mu}{dN}$ , which is equal to  $\beta + 2\gamma N$ , can be written down for any value of the concentration  $N$ .

### Statement of Results.

The numerical results are summarised in Table II. The halides of potassium and sodium chloride have been studied with temperature differences of 24 degrees and 14 degrees (approximately) across the cell, the rest with 14 degrees only. Since the effect is found to be practically proportional to the temperature difference in those cases with a slight general tendency to become greater the steeper the temperature gradient the figures have been reduced to correspond exactly with differences of 24.00 degrees or 14.00 degrees. In Fig. 12 the concentration change  $\Delta N$  is plotted against  $N$  for the solutions of the potassium halides and sodium chloride.

The fractional change per degree  $\frac{1}{N} \frac{dN}{dT}$  has been plotted against the normality in Fig. 13 which summarises all the results obtained with solutions of electrolytes. Experiments with glycerine and cane sugar solutions show measurable concentration changes.

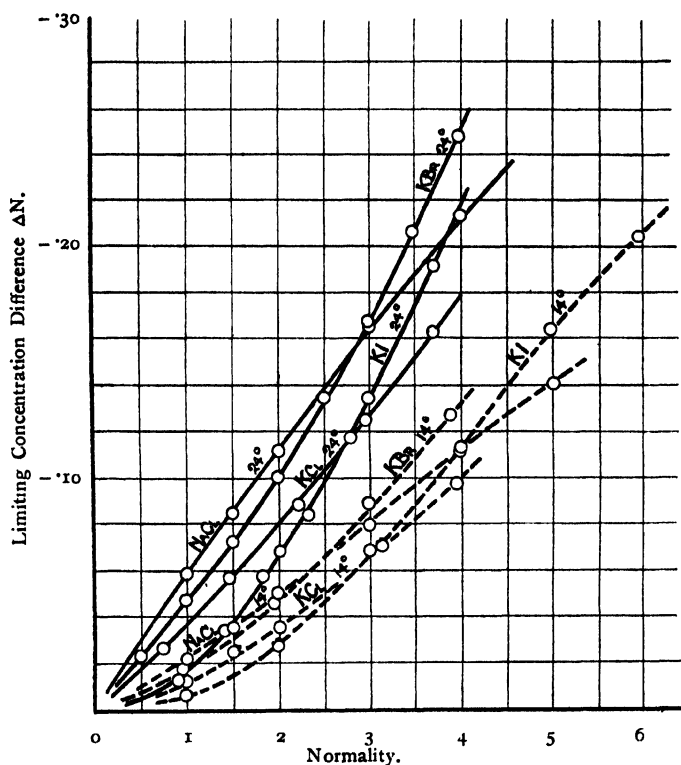


FIG. 12.

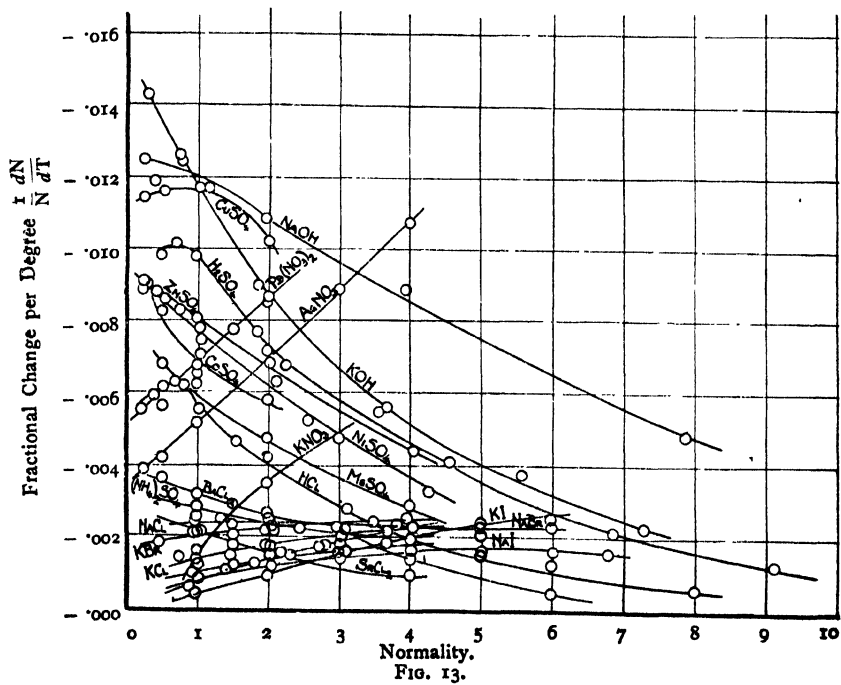


FIG. 13.

TABLE II.

Substance.	Normality.	Temperature Cent.			Reduced Temperature Difference.	$\frac{d\mu}{dN}$	$\Delta N$ .	$\frac{1}{N} \frac{dN}{dT}$
		Hot.	$\Delta T$ .	Cold.				
KCl	3'685	48'90	23'90	25'00	24'00	'00789	- '162	- '00188
	2'945	49'00	24'00	25'00	24'00	'00824	- '125	- '00177
	2'210	48'30	23'70	24'60	24'00	'00859	- '089	- '00168
	1'472	48'60	23'80	24'80	24'00	'00894	- '057	- '00161
	'738	48'90	23'70	25'20	24'00	'00928	- '026	- '00147
KBr	3'97	49'00	23'80	25'20	24'00	'01201	- '248	- '00260
	3'475	49'10	24'20	24'90	24'00	'01226	- '206	- '00247
	2'980	49'05	23'80	25'25	24'00	'01251	- '167	- '00233
	2'480	48'90	23'80	25'10	24'00	'01276	- '135	- '00226
	1'986	48'90	23'90	25'00	24'00	.01301	- '100	- '00210
	1'490	48'85	23'85	25'00	24'00	'01326	- '0715	- '00200
	'993	49'05	23'85	25'20	24'00	'01350	- '049	- '00206
	'497	49'05	23'90	25'15	24'00	'01375	- '0225	- '00188
KI	3'71	48'35	23'70	24'65	24'00	'01932	- '191	- '00214
	2'995	49'00	23'90	25'10	24'00	'01972	- '134	- '00186
	2'78	49'00	23'93	25'07	24'00	'01984	- '117	- '00175
	2'315	49'10	24'05	25'05	24'00	'02010	- '0835	- '00150
	1'994	49'00	23'85	25'15	24'00	'02028	- '0685	- '00143
	1'854	48'80	23'80	25'00	24'00	'02037	- '0585	- '00131
	1'396	49'00	23'90	25'10	24'00	'02062	- '0354	- '00106
	'928	48'70	23'70	25'00	24'00	'02088	- '0139	- '00062
NaCl	3'970	49'00	23'70	25'30	24'00	'00821	- '213	- '00223
	2'98	49'00	23'65	25'35	24'00	'00860	- '166	- '00232
	1'98	48'90	23'60	25'30	24'00	'00899	- '112	- '00234
	1'49	48'70	23'50	25'20	24'00	'00918	- '085	- '00237
	'99	48'80	23'60	25'20	24'00	'00937	- '059	- '00248
KCl	3'985	37'90	13'40	24'50	14'00	'00775	- '097	- '00173
	3'12	38'50	13'30	25'20	14'00	'00816	- '070	- '00166
	1'994	37'90	13'70	24'20	14'00	'00869	- '036	- '00129
	1'560	38'40	13'70	24'70	14'00	'00889	- '024	- '00110
	'997	37'90	13'90	24'00	14'00	'00916	- '0131	- '00094
KBr	3'85	37'90	14'10	23'80	14'00	'01217	- '127	- '00235
	3'00	41'00	14'20	26'80	14'00	'01250	- '0896	- '00213
	1'926	37'80	14'02	23'78	14'00	'01304	- '046	- '00170
	'964	38'00	13'90	24'10	14'00	'01352	- '018	- '00133
KI	6'00	40'60	14'50	26'10	14'00	'01828	- '203	- '00241
	5'00	40'60	14'30	26'30	14'00	'01860	- '163	- '00231
	3'99	38'10	14'30	23'80	14'00	'01916	- '111	- '00198
	3'00	41'00	14'25	26'75	14'00	'01972	- '068	- '00162
	1'994	38'20	14'30	23'90	14'00	'02028	- '0266	- '00095
	'997	38'10	14'10	24'00	14'00	'02084	- '0062	- '00045
NaCl	5'00	40'60	14'15	26'45	14'00	'00782	- '141	- '00201
	4'00	37'90	13'90	24'00	14'00	'00820	- '114	- '00203
	3'00	38'90	13'75	25'15	14'00	'00859	- '0790	- '00188
	2'00	38'80	13'85	24'95	14'00	'00898	- '0495	- '00177
	1'50	40'40	13'95	26'45	14'00	'00917	- '0358	- '00170
	1'00	40'40	14'05	26'35	14'00	'00936	- '0204	- '00146

## THE SORET EFFECT

TABLE II. (Continued).

Substance.	Normality.	Temperature Cent.			Reduced Temperature Difference.	$\frac{d\mu}{dN}$	$\Delta N$ .	$\frac{1}{N} \frac{dN}{dT}$ .
		Hot.	$\Delta T$ .	Cold.				
NaBr	6'00	40'70	14'10	26'60	14'00	'01151	- '198	- '00236
	5'00	40'60	14'30	26'30	14'00	'01184	- '166	- '00237
	4'00	38'70	13'70	25'00	14'00	'01217	- '134	- '00239
	3'00	38'80	13'65	25'15	14'00	'01249	- '0952	- '00227
	2'00	38'80	13'87	24'93	14'00	'01282	- '0600	- '00214
	1'00	41'20	14'00	27'20	14'00	'01315	- '0289	- '00206
NaI	6'74	40'60	14'20	26'40	14'00	'01911	- '132	- '00140
	6'00	40'70	14'30	26'40	14'00	'01942	- '1265	- '00150
	5'00	40'70	14'00	26'70	14'00	'01965	- '116	- '00166
	4'00	41'40	14'00	27'40	14'00	'01987	- '096	- '00172
	3'00	41'00	14'00	27'00	14'00	'02010	- '064	- '00152
	2'00	41'20	14'20	27'00	14'00	'02032	- '0337	- '00120
	1'00	41'00	14'10	26'90	14'00	'02055	- '0110	- '00079
BaCl <sub>2</sub>	3'012	38'50	14'25	23'25	14'00	'01288	- '1010	- '00239
	2'008	38'05	14'10	23'95	14'00	'01359	- '0742	- '00204
	1'004	38'05	14'05	24'00	14'00	'01429	- '0454	- '00323
	'500	40'60	14'10	26'50	14'00	'01465	- '0259	- '00370
SrCl <sub>2</sub>	4'00	38'10	14'00	24'10	14'00	'01147	- '0558	- '00099
	2'00	38'10	14'00	24'10	14'00	'01263	- '042	- '00150
	1'00	38'00	14'00	24'00	14'00	'01321	- '0288	- '00206
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	4'07	38'10	14'20	23'90	14'00	'00771	- '128	- '00224
	2'035	38'05	14'20	23'85	14'00	'00917	- '0672	- '00235
	1'018	38'00	14'05	23'95	14'00	'0098	- '0400	- '00281
CdSO <sub>4</sub>	2'025	37'80	14'00	23'80	14'00	'01131	- '166	- '00585
	1'012	38'00	13'70	24'30	14'00	'01286	- '0972	- '00685
	'506	38'70	13'80	24'90	14'00	'01337	- '0582	- '00822
	'25	40'30	13'95	24'35	14'00	'01363	- '0318	- '00907
CoSO <sub>4</sub>	2'58	38'10	14'20	23'90	14'00	'01185	- '185	- '00512
	1'472	38'00	14'40	23'60	14'00	'01279	- '145	- '00702
	'736	37'95	14'20	23'75	14'00	'01341	- '0865	- '00840
CuSO <sub>4</sub>	2'012	37'50	13'00	24'50	14'00	'01259	- '286	- '01015
	1'006	37'95	14'00	23'95	14'00	'01330	- '167	- '01185
	'503	37'95	14'00	23'95	14'00	'01376	- '083	- '01180
	'25	40'30	14'15	26'15	14'00	'01399	- '0407	- '01160
MgSO <sub>4</sub>	4'04	37'85	14'40	23'45	14'00	'00875	- '167	- '00295
	2'02	38'45	14'90	23'55	14'00	'01023	- '134	- '00473
	1'01	38'30	14'80	23'50	14'00	'01097	- '0875	- '00617
	'50	40'20	13'80	26'40	14'00	'01143	- '0483	- '00687
NiSO <sub>4</sub>	4'350	38'15	14'60	23'55	14'00	'01126	- '202	- '00332
	2'175	37'70	14'20	23'50	14'00	'01284	- '193	- '00638
	1'086	37'45	13'80	23'65	14'00	'01362	- '114	- '00750
	'50	40'30	13'80	26'50	14'00	'01403	- '0602	- '00860
ZnSO <sub>4</sub>	4'07	37'90	14'10	23'80	14'00	'01047	- '242	- '00425
	2'035	38'00	14'20	23'80	14'00	'01210	- '198	- '00695
	1'017	38'10	14'30	23'80	14'00	'01293	- '111	- '00780
	'407	38'40	14'50	23'90	14'00	'01342	- '0495	- '00870
	'25	40'30	14'10	36'20	14'00	'01354	- '0313	- '00895
Na <sub>2</sub> SO <sub>4</sub>	1'990	38'40	14'40	24'00	14'00	'00800	- '237	- '00850
	'999	38'10	14'30	23'80	14'00	'00927	- '111	- '00800
	'499	38'00	14'30	23'70	14'00	'00990	- '0384	- '00550
K <sub>2</sub> SO <sub>4</sub>	'990	38'50	14'60	23'90	14'00	'00883	- '0835	- '00595
	'495	38'30	14'40	23'90	14'00	'00977	- '0300	- '00430

TABLE II. (Continued).

Substance.	Normality.	Temperature Cent.			Reduced Temperature Difference.	$\frac{d\mu}{dN}$ .	$\Delta N$ .	$\frac{1}{N} \frac{dN}{dT}$ .
		Hot.	$\Delta T$ .	Cold.				
$H_2SO_4$	9.130	40.50	14.30	26.20	14.00	.00423	-.162	-.00127
	7.16	38.85	13.90	24.85	14.00	.00447	-.205	-.00205
	6.78	40.60	14.45	26.15	14.00	.00451	-.208	-.00219
	4.52	40.50	14.40	26.10	14.00	.00479	-.259	-.00409
	3.58	38.80	13.90	24.90	14.00	.00447	-.278	-.00554
	2.26	40.50	14.25	26.25	14.00	.00506	-.213	-.00672
	1.79	38.80	13.85	23.95	14.00	.00512	-.195	-.00777
	1.00	40.50	14.30	26.20	14.00	.00522	-.138	-.00985
	.716	38.80	13.80	24.00	14.00	.00525	-.103	-.01027
	.500	40.40	14.16	26.24	14.00	.00528	-.068	-.00970
HCl	8.00	40.60	14.65	25.95	14.00	.00605	-.068	-.00062
	6.00	40.50	14.40	26.10	14.00	.00663	-.100	-.00119
	5.00	40.60	14.35	26.25	14.00	.00693	-.107	-.00153
	4.00	40.70	14.30	26.40	14.00	.00723	-.127	-.00227
	3.20	38.30	13.60	24.70	14.00	.00747	-.129	-.00288
	2.85	40.70	14.25	26.45	14.00	.00757	-.122	-.00306
	2.00	40.60	14.30	26.30	14.00	.00783	-.117	-.00417
	1.60	38.70	13.95	24.75	14.00	.00795	-.105	-.00468
	1.00	40.60	14.20	26.40	14.00	.00812	-.078	-.00557
	.80	38.80	13.95	24.85	14.00	.00819	-.0710	-.00633
	.75	40.70	14.40	26.30	14.00	.00820	-.067	-.00637
	.50	40.50	14.20	26.30	14.00	.00827	-.047	-.00671
	.32	38.80	13.90	24.90	14.00	.00832	-.0264	-.00587
	.25	40.60	14.20	26.40	14.00	.00833	-.019	-.00543
$AgNO_3$	4.00	40.80	14.40	26.40	14.00	.01560	-.602	-.01075
	3.00	40.70	14.60	26.10	14.00	.01609	-.373	-.00890
	2.00	40.80	14.10	26.70	14.00	.01654	-.200	-.00715
	1.00	40.80	14.15	26.65	14.00	.01700	-.0723	-.00517
	.50	40.60	14.35	26.25	14.00	.01722	-.0296	-.00423
	.25	40.70	14.15	26.55	14.00	.01733	-.01385	-.00396
$Pb(NO_3)_2$	2.00	40.80	14.20	26.60	14.00	.01748	-.241	-.00860
	1.50	40.90	14.10	26.80	14.00	.01783	-.1630	-.00775
	1.00	40.60	13.80	26.80	14.00	.01818	-.0915	-.00655
	.50	40.80	13.90	26.90	14.00	.01853	-.0422	-.00602
$KNO_3$	3.00	39.00	13.90	25.10	14.00	.00716	-.204	-.00486
	2.00	40.60	13.90	24.70	14.00	.00776	-.0987	-.00352
	1.50	38.90	13.95	24.95	14.00	.00806	-.0612	-.00291
	1.41	37.90	14.05	23.85	14.00	.00811	-.0441	-.00223
	1.00	37.90	14.10	23.80	14.00	.00830	-.0170	-.00122
$NaNO_3$	6.00	40.50	15.30	26.20	14.00	.00556	-.3900	-.00465
	4.00	39.00	13.95	25.05	14.00	.00676	-.2260	-.00403
	3.00	38.80	13.90	24.90	14.00	.00731	-.1500	-.00356
	2.00	39.00	13.75	25.25	14.00	.00790	-.0810	-.00290
	1.00	38.90	13.80	25.10	14.00	.00848	-.0190	-.00136
$NH_4NO_3$	8.00	40.40	13.95	26.45	14.00	.00716	-.268	-.00239
	6.00	40.40	14.05	26.35	14.00	.00789	-.162	-.00192
	4.00	40.25	13.90	26.35	14.00	.00863	-.0517	-.00095

## THE SORET EFFECT

TABLE II. (Continued).

Substance.	Normality.	Temperature Cent.			Reduced Temperature Difference.	$\frac{d\mu}{dN}$ .	$\Delta N$ .	$\frac{1}{N} \frac{dN}{dT}$ .
		Hot.	$\Delta T$ .	Cold.				
KOH	7'33	40'30	13'85	26'45	14'00	'00708	-'244	-'00238
	5'54	40'30	13'80	26'50	14'00	'00783	-'297	-'00384
	3'66	40'30	13'60	26'70	14'00	'00859	-'284	-'00553
	1'83	40'20	13'85	26'35	14'00	'00935	-'231	-'00900
	1'108	40'30	13'75	26'55	14'00	'00965	-'183	-'01183
	'692	40'70	13'95	26'75	14'00	'00987	-'122	-'01260
	'277	40'40	13'85	26'55	14'00	'00999	-'055	-'01420
NaOH	7'93	40'50	14'15	26'35	14'00	'00440	-'539	-'00486
	3'965	40'20	13'95	26'25	14'00	'00730	-'488	-'00880
	1'983	40'40	14'05	26'35	14'00	'00875	-'300	-'01080
	'793	40'50	14'00	26'50	14'00	'00962	-'139	-'01250
	'397	40'40	14'00	26'40	14'00	'00991	-'066	-'01190
	'198	40'50	13'90	26'60	14'00	'01025	-'035	-'01260
Glycerine	6'00	48'65	25'00	23'65	24'00	'01060	-'0649	-'00046
	4'00	48'90	25'50	23'40	24'00	'01060	-'139	-'00145
	3'00	49'15	25'00	24'15	24'00	'01050	-'153	-'00213
	2'00	48'75	25'50	23'25	24'00	'01040	-'123	-'00256
	1'00	48'80	25'00	23'80	24'00	'01040	-'0615	-'00256
Cane Sugar	1'00	49'40	25'00	24'40	24'00	'04800	-'0348	-'00145
	'50	49'33	24'50	24'83	24'00	'04700	-'0251	-'00209
	'25	49'30	24'50	24'80	24'00	'04700	-'0120	-'00200
	1'27 '883	38'30 38'70	13'70 13'90	24'60 24'80	14'00 14'00	'04800 '04800	-'011 -'015	-'00062 -'00121

Calcium chloride	4'20 N.	Very small changes.
	2'10 N.	
	1'05 N.	
Magnesium chloride	3'69 N.	"
	1'84 N.	
	0'92 N.	
Lithium chloride	10'00 N.	"
	4'00 N.	
	2'00 N.	
Ammonium chloride	1'00 N.	"
	4'00 N.	
	3'00 N.	
Lithium sulphate	1'00 N.	"
	4'00 N.	
	1'00 N.	"

With these solutions in the cell successive exposures gave practically coincident lines on the plate.

### Conclusion.

An optical method of measuring the "Soret Effect" in solutions has been applied to the measurement of the effect in fairly concentrated solutions of electrolytes. General agreement is found between the results here recorded and the most reliable of those of previous workers.

Whilst this paper was in preparation, a paper by John Chipman has appeared which deals with the measurement of the effect by a conductivity method in solutions of electrolytes. His results for HCl solutions show a maximum effect at about 1 normal with a diminishing effect at high and extremely low concentrations. The figures tabulated above bear out this

result. The low effects of Li and  $\text{NH}_4$  salts in solution and the great effect of hydroxyl compounds such as KOH and NaOH are also confirmed. The magnitude of the fractional change per degree found by the optical method is, however, always numerically greater than that found by the conductivity method. It does not seem that this is due entirely to the different temperature gradients used.

The author wishes to express his thanks to Professor F. G. Donnan, at whose suggestion the work was commenced, and also to thank Messrs. Adam Hilger, Ltd., for invaluable assistance in the construction of apparatus and the Department of Scientific and Industrial Research for a grant which has enabled the work to be done.

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**Dr. Borns** asked whether the Schlieren, or striac photographic method of Toepler would not be more convenient than direct photography. The Toepler method had been found very useful in determining changes in the pressure and density of the air round flying bullets.

**The President** remarked on the interest of the measurements contained in the paper and on the extremely ingenious method of measuring the changes of concentration over such a small distance. The Soret effect was of great interest to metallurgists at the present time. In discussions on segregation in steel ingots it had been suggested by Professor C. Benedicks and also by the Ingots Committee of the Iron and Steel Institute that the Soret effect was capable of producing the changes in concentration observed in different parts of an ingot. He found on calculation that, if the concentration were approximately proportional to the absolute temperature, differences of temperature of several hundred degrees would be necessary to produce the observed effect. In the light of Mr. Tanner's experiments the effect seemed too small to have any appreciable influence on ingot segregation.

**The Author**, in reply to Dr. Borns, said this method could not conveniently be used for the analysis of a solution, the refractive index of which diminished uniformly with the height. He thanked the President for directing his attention to the paper by Carl Benedicks on "The Hot Wall," in which there is a reference to the work of A. Eilert on the "Ludwig-Soretische Phänomen."

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## VAPOUR PRESSURE AND HEAT OF DILUTION OF AQUEOUS SOLUTIONS, PART IV. AN IMPROVED METHOD OF MEASURING VAPOUR PRESSURE BY AIR BUBBLING.

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The method of determining vapour pressures of liquids by air bubbling has been tried by various workers. Reference to the work of the following serves to illustrate the diversity of the methods employed, and the difficulties to be overcome—Perman,<sup>1</sup> Kahlenberg,<sup>2</sup> Lincoln and Klein,<sup>3</sup> Krauskopf,<sup>4</sup>

<sup>1</sup> *Proc. Roy. Soc.*, 1903, **72**, 72.

<sup>2</sup> *J. Physical Chem.*, 1907, **12**.

<sup>3</sup> *Science*, July 31st, 1905.

<sup>4</sup> *Ibid.*, 1910, **14**.

Daniels, Derby, and Gutsche.<sup>1</sup> With these should also be associated the work of Berkeley,<sup>2</sup> whose modification of the air-bubbling method by the "Rocking Method" is now well known. The difficulties involved in this method are such that many of the results of these experiments are erroneous and the method has consequently received severe criticism.

A theoretical objection has been raised against the method by Callendar,<sup>3</sup> and later by Orson Wood,<sup>4</sup> who suggest that an error of some consequence occurs by the assumption that steam behaves as an ideal gas. In the air-bubbling method we are dealing with a mixture of air and water vapour and, in most cases, the air is present in much greater proportion than the water vapour. For such a mixture the work of Perman<sup>1</sup> shows clearly that the errors involved in such an assumption are small enough to be neglected. It is shown in this paper that the two assumptions made in calculating vapour pressures, *viz.*, that Dalton's Law of partial pressures is valid and that the density of aqueous vapour is normal, are either justified or that the errors are balanced. The latter conclusion is unlikely and is negated by the work of other investigators who have measured these deviations. At a temperature of 90° C. and upwards, when the water vapour is present in good proportion to the air, the errors increase and a correction might be made; but the air-bubbling method is not suitable for measuring large vapour pressures at high temperatures on account of other factors. The objection therefore requires more support and evidence.

The method used was essentially the same as that employed by Perman,<sup>1</sup> but with many improvements and safeguards, *viz.* :—

(1) In order to ensure saturation of the air, *four* bubblers were used instead of *three*.

(2) The bubblers were shaped differently, being broader at the bottom. They had a small bulb at the top to break up any septa formed by the bubbling (these were however not observed).

(3) A wide tube, 25 cm. long by 2.5 cm. in diameter, was fixed at the outlet from the bubblers to act as a condensation chamber, so that the air, if supersaturated or containing spray in suspension, might become normal.

(4) The tap forming the dividing point between the saturated vapour and the dry air was placed *inside* the bath.

(5) *Three* absorption bulbs were used instead of two.

(6) The tube for saturating the air before measuring its volume was placed in the same bath as the aspirator.

(7) The bath in which the aspirator was placed was surrounded by a cardboard box packed with cotton wool, and the temperature of the bath was read through a glass window.

(8) The rate of aspiration was reduced to about 1 litre per hour.

The most important of these improvements are the condensation chamber and the tap.

*The Three-Way Tap.*—The method previously used consisted in including in the train an ordinary three-way tap, fused on to the last saturating bubbler, and placed outside the bath. To prevent condensation of vapour on the walls of the tube, gas-heated copper tubes were placed around the exposed tubes of the tap. This permitted errors in two directions. Moisture might be deposited in the tube in the barrel of the tap; secondly the copper heated tubes might so heat up the lubricant of the tap that a little of the latter would run back to the last bubbler and there prevent accurate measurement of vapour pressure. To obviate this, two

<sup>1</sup> *J. Amer. Chem. Soc.*, 1914, 36.

<sup>2</sup> *Trans. Faraday Soc.*, 1913, 8.

<sup>3</sup> *Phil. Trans.*, 1909, A 209.

<sup>4</sup> *Ibid.*, 1915, 11.

arrangements were devised, both of which proved very satisfactory. Both are designed to work inside the thermostat and to avoid the use of grease, which, we find, is the cause of much error in vapour pressure measurements.

The one which was used throughout for the measurements of vapour pressures of sucrose solutions consists essentially of two double U tubes suitably attached. An approximately half-scale drawing of this form of three-way tap is shown in Fig. 1. The main U tube "A" is attached at its one end to the saturator, at the other end to the absorption bulbs. At the top of the second limb "C" the U tube "B" is attached, its free end being connected to the air drying train. U tubes "A" and "B" each have

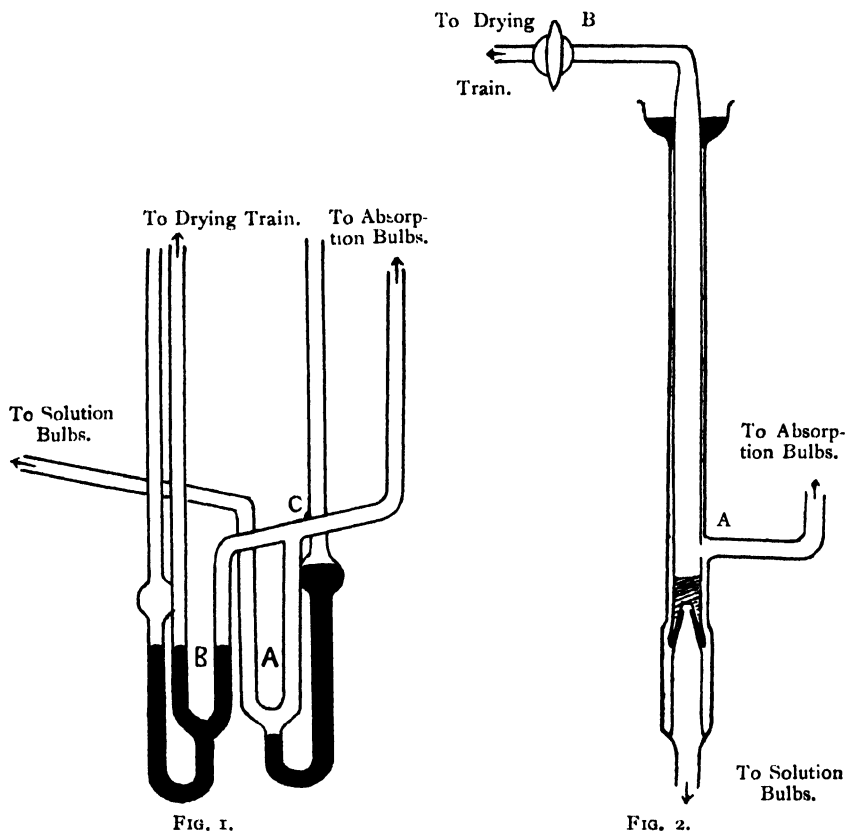


FIG. 1.

FIG. 2.

tubes fused on at their bases; these emerge from the bath and are closed at their free ends by screw clips. These tubes are provided, near the bottom, with a bulb to prevent the mercury from rising above the level of the water in the thermostat. By suction of mercury out of "A," direct connection between saturator and absorber is made. Suction out of "B" gives connection from drying train to absorption bulb. The point "C" may be regarded as the stop point in the apparatus. An objection arises in that the air passing over the mercury surface may become saturated with mercury vapour. Assuming saturation with mercury vapour at  $80^{\circ}\text{C}$ ., the highest temperature at which measurements were made, we find that the amount of mercury so collected in the sulphuric acid would be 0.00005 gramme, so that the error is negligible.

## 98 MEASURING VAPOUR PRESSURE BY AIR BUBBLING

A second arrangement has been devised and gave, when tested, equally good results. A diagram of the apparatus is shown in Fig. 2. With the inner tube raised, connection is made between the bubblers and absorption bulbs; with the inner tube lowered, this connection is stopped and aspiration is only possible through the tap "B" to the absorption vessel. The "stop point" here is at the glass joint "A." Mercury is placed in the outer tube so as to form a seal for this joint and to avoid the use of grease.

The tube emerging from the thermostat and running to the absorption bulbs has to be heated to prevent condensation of moisture. For this purpose a suitable wire is wound round asbestos cord on the glass tube, a variable high resistance included in the circuit and the tube thus heated electrically.

### Measurement of Pressure and Temperature.

Instead of mercury, highly purified liquid paraffin was used in an open gauge. This gauge is drawn out to a capillary at its open end, which has the effect of considerably damping oscillations due to bubbling. It is connected to the aspirator through a tap and capillary tube and lies in front of a mirror scale. Careful experiments showed that it does not take up water vapour and that its own vapour pressure is quite negligible. It was only in contact with the aspirator for about five minutes during an experiment and the tap was then closed. Careful density determinations gave a value of  $\cdot 8982$  gm. per c.c., and this corresponds to a factor of  $13\cdot 13$  in order to convert pressure readings to millimetres of mercury. In each experiment two readings on this gauge are necessary; the pressure difference on aspirating through absorption and saturating bulbs which we may term  $p$  and the pressure difference, on aspirating through absorption bulbs only,  $p_1$ . All the barometric readings were made by reading the barometer with a cathetometer capable of reading to one hundredth of a millimetre; these readings were reduced to  $0^\circ \text{C}$ .

Temperatures in the aspirator were taken to the nearest tenth of a degree and were read with a good lens.

The regulation of temperature in the thermostat was effected by a specially devised thermo-regulator in which the tube containing the toluene runs in turn parallel to the four walls of the thermostat. It kept the temperature constant to one hundredth of a degree.

The apparatus has been subjected to a rigorous test by the determination of the vapour pressures of water at a number of temperatures according to the method indicated above. The temperatures ranged from  $40^\circ \text{C}$ . to  $80^\circ \text{C}$ . The vapour pressures were calculated in the way described by Perman.<sup>1</sup>

### The Vapour Pressures of Water at Various Temperatures.

Vapour pressures are given in millimetres. The deviations given are the mean deviations for the temperatures concerned and are in mm. of mercury.

The mean percentage deviation from Regnault's corrected values (taken from *Physiko-chemische Messungen*—Ostwald Luther) is so small, that the method of measuring vapour pressures by air bubbling evidently can be made to give quite as accurate values as those obtained by other means over a range of temperatures.

No.	Temp. of Water, ° C.	Vapour Pressure Calculated.	Regnault's Value.	Mean Deviation.
1.	39°95	54°80 mm.	55°02 mm. }	·195 mm.
2.	40°00	55°33	55°16	
3.	50°00	92°30	92°35 }	·13
4.	50°08	92°87	92°72	
5.	50°10	93°00	92°82	
6.	60°01	149°4	149°39 }	·07
7.	60°01	149°4	149°39	
8.	60°02	149°6	149°40	
9.	60°16	150°5	150°44	
10.	65°05	187°9	188°00 }	·165
11.	65°07	188°4	188°17	
12.	70°00	234°0	233°8 }	·195
13.	70°00	233°9	233°8	
14.	69°98	233°3	233°39	
15.	75°00	289°5	289°3	·20
16.	79°93	354°5	354°4 }	·14
17.	80°08	356°7	356°5	
18.	79°83	353°2	353°32	
19.	79°83	353°3	353°32	
20.	79°84	353°2	353°46	

### The Vapour Pressures of Aqueous Sucrose Solutions.

Although the determination of vapour pressures of these solutions has been tried by several investigators, an investigation of vapour pressures over a range of temperatures and concentrations is lacking. Berkeley and Hartley<sup>6</sup> have measured the vapour pressures of these solutions at 0° C. and 30° C. for the purpose of calculating osmotic pressures. Their results, obtained by a dynamical method, are probably very accurate. Perman and Price<sup>9</sup> have measured the vapour pressures of some solutions at 70° C. and 90° C. Their results have been criticised as being not as accurate as is desirable. Orson Wood<sup>8</sup> has measured the vapour pressures of three sugar solutions at temperatures ranging from 60° C. to 90° C. The accuracy claimed for the results is to within one part in two hundred. An objection which seems of some importance is the presence of a small amount of grease in the solution. This grease might easily be introduced in the filling process by the contact of the hot solution with glass taps; it is significant that all Orson Wood's test experiments on the vapour pressures of water give low values compared with Regnault's corrected values. At 90° C. his value is three millimetres lower than Regnault's. Such errors seriously diminish the practical value of the work and render many of the conclusions unconvincing.

Perman and Saunders<sup>10</sup> have investigated the vapour pressures of sugar solutions over a range of concentrations at two temperatures, 70° C. and 90° C. by a static method. This work suffers from no serious theoretical

<sup>9</sup> *Trans. Faraday Soc.*, 1912, 8, 1.

<sup>10</sup> *Ibid.*, 1923, 19.

or practical objections and the results serve to a limited extent as a comparison against those given hereunder.

The estimation of the concentration of the solution needs mention. All sugar solutions were made from purified cane sugar and well boiled redistilled water. In the early stages of the work the sugar and water were carefully weighed out and the weighed concentration was thus obtained. In determining the densities of these solutions, it was noticed by plotting density of solution against weight concentration that the relation approximates to a linear function. This is still more marked when density is plotted against volume concentration: from such a smooth curve the concentration of a solution may be estimated accurately by taking a density of the solution and reading off from the curve. This method was adopted for estimating the remainder of the sucrose solutions. The accurate density determinations present no great difficulty and the densities, over the range of concentrations at which vapour-pressures have been measured, were determined at all seven temperatures. It is necessary to take a density determination of the solution in the bulbs at the working temperature and so obtain from the curve the required concentration. The error in the density determinations was not more than one part in a thousand. Densities of aqueous sugar solutions have been measured by Plato<sup>11</sup> from 0° C. up to 60° C. and our values show good agreement with his. The experimental results obtained on the densities and vapour pressures of these solutions are given in the succeeding tables. Concentration is given in grams per 100 c.c. of solution.

#### THE DENSITIES OF AQUEOUS SUCROSE SOLUTIONS.

Two pycnometers were used, one of about 10 c.c. capacity, and the other a little over 7 c.c. The results are here tabulated. From the numbers given the weight concentration and the value of  $\frac{N}{N}$  can be calculated if required.

40°.		50°.		60°.		65°.		70°.		75°.		80°.	
Concentration.	Density.	Concentration.	Density.	Concentration.	Density.	Concentration.	Density.	Concentration.	Density.	Concentration.	Density.	Concentration.	Density.
8.608	1.025	8.574	1.021	8.533	1.016	9.348	1.016	8.482	1.010	9.283	1.009	5.697	.994
17.42	1.059	17.32	1.053	17.26	1.049	19.73	1.056	10.10	1.016	19.57	1.047	10.12	1.010
25.75	1.087	25.64	1.082	21.79	1.064	27.77	1.085	17.17	1.044	27.72	1.083	19.16	1.045
35.98	1.128	35.83	1.123	25.53	1.077	32.90	1.104	25.40	1.072	32.73	1.098	26.33	1.072
46.70	1.167	46.49	1.162	35.63	1.117	42.85	1.142	29.20	1.090	42.63	1.136	35.34	1.106
57.15	1.207	56.87	1.201	42.47	1.141	54.83	1.184	35.44	1.111	54.50	1.177	44.48	1.140
65.98	1.236	65.64	1.231	46.17	1.154	70.86	1.246	45.97	1.149	70.58	1.241	53.93	1.176
81.06	1.293	80.61	1.286	56.54	1.194	86.06	1.302	56.27	1.188	85.67	1.296	69.92	1.229
90.80	1.329	90.38	1.323	65.34	1.225	88.76	1.309	64.91	1.217	88.59	1.307	78.11	1.265
—	—	—	—	80.37	1.282	—	—	79.82	1.273	—	—	94.61	1.322
—	—	—	—	89.97	1.317	—	—	89.35	1.309	—	—	—	—

<sup>11</sup> *Abhdl. Norm. Eich. Komm.*, 1900, 2, 140.

## VAPOUR PRESSURES OF AQUEOUS SOLUTIONS OF SUCROSE.

40°.			50°.			60°.			65°.		
Concentration.	Density.	V.P.	Concentration.	Density.	V.P.	Concentration.	Density.	V.P.	Concentration.	Density.	V.P.
0°0	—	55°16	0°0	—	92°35	0°0	—	149°3	0°0	—	187°5
10°53	1°032	54°54	10°51	1°028	91°79	12°88	1°0325	148°55	19°72	1°055	185°7
11°40	1°036	54°27	22°32	1°073	91°74	19°84	1°059	147°9	27°97	1°086	184°8
23°16	1°082	54°16	27°25	1°090	91°07	30°92	1°099	146°8	39°78	1°129	188°5
35°26	1°124	53°55	27°49	1°091	90°51	30°92	1°099	146°6	51°30	1°174	178°5
47°32	1°169	53°04	36°04	1°139	89°55	42°20	1°141	144°7	62°33	1°212	174°2
61°80	1°223	51°77	46°15	1°161	88°81	52°81	1°180	142°3	62°63	1°213	175°2
64°63	1°233	51°33	51°13	1°179	88°45	60°82	1°2095	140°1	77°80	1°269	168°2
69°24	1°250	51°22	53°46	1°188	88°20	75°41	1°2625	134°7	84°89	1°295	164°1
69°24	1°250	51°16	55°94	1°197	87°52	82°45	1°289	132°1	100°90	1°357	147°1
78°02	1°282	50°00	65°22	1°230	85°88	82°45	1°289	131°8	In the last experiment at 60° the solution was at the point of saturation, as sugar crystallised out in the first bubbler during the experiment.		
78°02	1°282	50°12	73°24	1°263	83°51	89°58	1°316	128°2			
93°26	1°338	46°51	85°07	1°303	80°88	89°58	1°316	128°1			
—	—	—	93°07	1°332	76°92	93°63	1°331	124°7			
—	—	—	—	—	—	93°63	1°331	124°7			
—	—	—	—	—	—	103°9	1°3715	113°8			

70°.			75°.			80°.		
Concentration.	Density.	Vapour Pressure.	Concentration.	Density.	Vapour Pressure.	Concentration.	Density.	Vapour Pressure.
0°0	—	233°8	0°0	—	289°3	0°0	—	355°4
8°12	1°0095	233°1	11°09	1°017	288°2	7°30	1°000	354°4
11°08	1°024	232°9	21°57	1°057	285°7	21°19	1°052	352°0
11°98	1°024	232°9	27°28	1°078	284°9	27°17	1°075	350°8
17°11	1°044	231°4	27°28	1°078	284°6	37°43	1°113	347°0
17°11	1°044	231°5	37°58	1°116	281°5	41°45	1°128	345°8
17°11	1°044	231°5	40°71	1°128	281°2	49°97	1°160	342°1
23°52	1°0675	230°3	50°69	1°165	277°2	59°34	1°194	335°7
23°52	1°0675	230°2	58°34	1°192	273°7	64°06	1°211	333°6
31°79	1°0975	228°7	70°86	1°237	266°1	65°22	1°215	332°4
31°79	1°0975	228°8	78°20	1°265	257°7	68°84	1°228	328°7
41°46	1°134	226°8	81°43	1°277	255°3	74°42	1°248	324°1
41°46	1°134	226°8	85°15	1°292	250°8	74°42	1°248	324°5
49°65	1°159	224°7	—	—	—	79°34	1°267	314°8
49°65	1°159	224°1	—	—	—	79°34	1°267	314°8
60°99	1°204	219°9	—	—	—	81°28	1°274	313°6
60°99	1°204	220°2	—	—	—	83°83	1°286	308°8
73°10	1°2475	214°1	—	—	—	86°88	1°296	307°2
73°10	1°2475	213°9	—	—	—	92°76	1°319	294°4
84°43	1°296	203°3	—	—	—	92°76	1°319	294°1
85°70	1°296	202°8	—	—	—	—	—	—
85°70	1°296	202°5	—	—	—	—	—	—

In some cases especially at 70°, two or three experiments were carried out under identical conditions; it will be seen that the agreement in the vapour pressure results is usually extremely good.

All these results have been plotted as isothermal curves, and are very concordant. At the lower temperatures there are a few deviations of 0·5

mm. from the curve whilst at 70° and above there are a few deviations of 1 mm. and one or two a little more.

On comparing these results with those of Orson Wood<sup>8</sup> considerable discrepancies are found. Orson Wood measured vapour pressures from 60° to 90°, but for only three concentrations. The corresponding vapour pressures read from our own curves, together with Orson Wood's, are given below :—

	$\frac{n}{N}$	60°.	65°.	70°.	75°.	80°.
Downes and Perman . . .	·0824	134·0	168·1	211·0	260·1	319·5
Orson Wood . . . . .	·0824	131·9	166·8	208·4	257·5	316·8
Downes and Perman . . .	·1182	127·4	158·7	—	—	298·4
Orson Wood . . . . .	·1182	118·7	150·2	—	—	291·6

At the higher concentration the discrepancy amounts to over 8 mm. ; the numbers are always lower than ours. We would suggest as the cause of the error that the mercury column exposed to the air is very difficult to correct for temperature, and grease from the stopcock may have lowered the vapour pressure.

We wish to point out that in our tests with water (20 experiments), the deviation from Regnault's numbers is greater than 0·2 mm. in three experiments only and the mean deviation (reckoning all as if of the same sign) is 0·14 mm. In Orson Wood's test, however, the deviation from Regnault's numbers varies from 0·2 mm. to 2·5 mm. and his numbers are always low. In support of our values we have the results of Perman and Saunders by a statical method.<sup>10</sup> At 70° a comparison is possible. The deviation of their points from our curve does not exceed 1·5 mm., and is usually much less, while the points are evenly distributed about the curve.

### The Osmotic Pressures of Aqueous Sucrose Solutions.

The exact relation connecting osmotic pressure and vapour pressure for solutions of any concentration and compressibility has been worked out by Porter.<sup>12</sup> He gives—

$$\int_{\pi_{\pi}}^p s dp = \int_{\pi_{\pi}}^{\pi_{\infty}} v dp + \int_{\pi_{\infty}}^{p-P_p} u dp \quad . \quad . \quad . \quad (1)$$

His equation is derived from consideration of ideal conditions which approximate to a vacuum; Berkeley, Hartley, and Burton<sup>6</sup> have modified his equation to give an expression suitable to the conditions of their actual experiments. They obtain :—

$$\int_{A+\pi_{\pi}}^{A+p} s dp = \int_{\pi_{\pi}}^{\pi_{a0}} v dp + \int_{A+\pi_{a0}}^{A+p_0} u dp \quad . \quad . \quad . \quad (2)$$

In these two equations the symbols have the following significance—

For the solution :—

Hydrostatic pressure on the solution :  $p$ .

Vapour pressure when solution is in contact with its own vapour :  $\pi_{\pi}$ .

Osmotic pressure for a hydrostatic pressure  $p$  :  $P_p$ .

*For the solvent:—*

Specific volume at a hydrostatic pressure  $p_0$ :  $v_{p_0}$ .

Vapour pressure when solvent is in contact with its own vapour:  $\pi_{00}$ .

Specific volume of vapour under various pressures:  $V_{\pi}$ , etc.

*In addition.* Atmosphere pressure:  $A$ .

Vapour pressure of solvent in air under a total pressure  $A + \pi_{a0}$ :  $\pi_{a0}$ .

Vapour pressure of solution in air under a total pressure  $A + \pi_{a\pi}$ :  $\pi_{a\pi}$ .

$s$ —the shrinkage in volume when one gram of solvent is removed from an infinite volume of solution.

Although equation (2) is strictly more applicable to the vapour pressures we have measured, both equations have been treated in order to calculate osmotic pressures. Both require a knowledge of the compressibilities of the solutions under consideration. Berkeley and Hartley have measured the compressibilities of these solutions over a wide range of concentrations at  $0^\circ$  C and  $30^\circ$  C. One of us has also measured them at two higher temperatures,  $70^\circ$  C and  $90^\circ$  C. It is found that in each case the compressibilities approximate to a linear function of the concentration and that the functions change very little in order of magnitude throughout. It is therefore a fairly easy task to obtain interpolated values from which the compressibilities of the solutions at the remaining temperatures we are considering can be read off with sufficient accuracy.

*Porter's Equation.*—To integrate we may assume that water vapour obeys Boyle's Law with sufficient accuracy for the purposes required here,

so that we obtain  $v = \frac{RT}{p}$ .

To allow for the compressibility of the liquid we may write  $s = s_0(1 - cp)$  where  $c$  is the compressibility of the solution. On integration the " $u$ " term disappears on inserting the limits, for  $P_p = p - \pi_{00}$  when the solvent is under its own vapour pressure. Thus we obtain—

$$ps_0 \left( 1 - \frac{cp}{2} \right) - \pi_{\pi}s_0 \left( 1 - \frac{c\pi_{\pi}}{2} \right) = RT \log_e \frac{\pi_{00}}{\pi_{\pi}}.$$

Rearranging,

$$P_p \left( 1 - \frac{cP_p}{2} \right) = \frac{RT}{s_0} \log_e \frac{\pi_{00}}{\pi_{\pi}} - (\pi_{00} - \pi_{\pi}) \quad (3)$$

all other terms being of negligible magnitude.

$s_0$  has been evaluated in this case by using the expression obtained by Callendar,<sup>13</sup>  $s = v - c \frac{dv}{dc}$ . Here  $v$  is the specific volume, and  $c$  is the concentration expressed as grams of solute to grams of solvent.  $v$  and  $\frac{dv}{dc}$  may be obtained from the density curves.

Proceeding in this way osmotic pressures of four solutions have been calculated at different temperatures from equation (3). Too much stress should not be laid on these results, or on those calculated by means of equation (2) (Berkeley and Hartley's) since, to make the calculations effective,

$\log_e \frac{\pi_{00}}{\pi_{\pi}}$  must be known far more accurately than our vapour pressures permit.

Errors in this expression are multiplied enormously in the final calculation. The osmotic pressures of four solutions are given in the table below. Concentrations are 20, 25, 45, and 60 grams of sucrose per 100 grams of solu-

tion respectively. The vapour pressure, the coefficient of compressibility, and " $s$ " for each solution is given at the different temperatures.

Concentration, g./100 g.	Temp. ° C.	$\pi_{\pi}$	Coefficient of Compressibility.	$s$ .	Osmotic Press. Atmos.
20	50	91.32	.0000390	1.0223	15.95
"	60	147.6	.0000395	1.028	17.17
"	70	231.15	.0000402	1.0327	17.74
"	80	351.4	.00004105	1.0405	17.88
25	50	90.8	.0000376	1.0195	24.33
"	60	146.9	.0000381	1.025	24.27
"	70	230.1	.0000387	1.0303	24.51
"	80	349.9	.0000395	1.038	24.33
45	40	52.4	.0000313	1.003	73.47
"	50	87.9	.0000318	1.0089	72.03
"	60	142.2	.0000323	1.0145	73.45
"	70	223.1	.0000330	1.0205	72.06
"	80	339.6	.0000337	1.0275	71.16
60	40	49.7	.00002675	0.995	150.2
"	50	83.1	.0000275	1.000	156.3
"	60	135.2	.0000280	1.006	151.1
"	70	211.9	.00002855	1.013	153.4
"	80	322.15	.0000294	1.0195	156.2

The values so obtained represent osmotic pressures calculated from points on the vapour pressure curves.

*Berkeley, Hartley and Burton's Equation.*—Their relation runs—

$$\int_{A + \pi_{a\pi}}^{A + p} s dp = \int_{\pi_{a\pi}}^{\pi_{a0}} v dp + \int_{A + \pi_{a0}}^{A + p_0} u dp$$

To integrate this equation we have proceeded on much the same lines as the authors themselves adopted.

We may write  $\bar{s}$  as the mean value of  $s$  between the limits concerned;  $\int_{A + \pi_{a\pi}}^{A + p} s dp$  this being now considered independent of pressure, the integral becomes  $\bar{s}(p - \pi_{a\pi})$ .  $\bar{s}$  has been found, as stated in their work, except that pressure ranges from 1-100 atmospheres are used for the dilute solutions and 1-200 atmospheres in the case of the concentrated solutions. Since they find the value for any solution varies with pressure at a maximum 0.5 per cent., this seems quite permissible.

Assuming Boyle's Law and Dalton's Law of Partial Pressures to apply to the water vapour in air, we obtain the following value for this  $\int_{\pi_{a\pi}}^{\pi_{a0}} v dp$  integral:  $\frac{\pi_{a0}}{\rho_{a0}} \log_e \frac{\pi_{a0}}{\pi_{a\pi}}$ .  $\rho_{a0}$  is the vapour density of water vapour in air when water is under a total pressure  $A + \pi_{a0}$ .

The third integral simply becomes  $-u\pi_{a0}$ , so that the osmotic pressure

$$P = \frac{\pi_{a0}}{760\bar{s}} \left( \frac{1}{\rho_{a0}} \log_e \frac{\pi_{a0}}{\pi_{a\pi}} - u \right) + \frac{\pi_{a\pi}}{760} \quad (4)$$

### Osmotic Pressures using Berkeley and Hartley's Equation.

$u$  = is the specific volume of water.

$\rho_{a0}$  = is the vapour density of water vapour in air when water is under a total pressure  $A + \pi_{a0}$

As these quantities vary only with temperature, and are the same for each solution, the values are only given for the first concentration.

$\bar{v}$  has the significance given above.

Concentration g./100 g.	Temp. ° C.	$\rho_{a_0}$	$\mu$	$\bar{v}$	Osmotic Pressure. Atmos.
20	40	·0000507	1·00773		
"	50	·0000823	1·01201	1·004	16·52
"	60	·0001291	1·01697	1·013	17·19
"	70	·0001963	1·02260	1·016	17·76
"	80	·0002901	1·02890	1·013	17·90
25	50			1·004	24·62
"	60			1·004	24·71
"	70			1·004	25·07
"	80			1·015	24·78
45	40			1·003	73·26
"	50			1·003	72·28
"	60			1·009	73·73
"	70			1·015	71·95
"	80			1·030	70·58
60	40			1·000	148·67
"	50			1·000	155·11
"	60			1·000	150·48
"	70			1·029	149·6
"	80			1·037	152·34

Before commenting on these results, we will give the osmotic pressures of these solutions on the assumption that we are dealing with an ideal solution. The equation is—

$$P = \frac{RT}{V_0} \left( -\log_e \frac{\pi_\pi}{\pi_0} \right) = \frac{RT}{V_0} \left( \frac{\pi_0 - \pi_\pi}{\pi_0} + \frac{\frac{1}{2}(\pi_0 - \pi_\pi)^2}{\pi_0} + \dots \right)$$

The osmotic pressures for a solution containing 25 grams sucrose per 100 grams of solution have been calculated using this equation, and values are given below.  $V_0$  is the specific volume of the solvent.

Temp. ° C.	$V_0$	Osmotic Pressure.
50	1·01201	24·62 atmos.
60	1·01697	24·38 "
70	1·02260	24·40 "
80	1·02890	24·39 "

We may now compare very briefly our results with those of other workers who have measured the osmotic pressures more directly. The values are tabulated below; the first three columns are calculated values, and the last four are the osmotic pressures of other workers measured directly.

Other noticeable points in our results are the small effect of temperature change and the close agreement of the numbers with those calculated from the ideal equation. A 25 per cent. solution can hardly be considered as ideal, yet the departure from ideal conditions appears to be but small. It must be remembered however that the sucrose molecule is a large one.

We are carrying out measurements of the heat of dilution over a considerable range of temperature and will consider these together with the effect of change of temperature in a later paper. On the whole the results here recorded are as concordant as could reasonably be expected.

Grams Sugar to 100 gms. Solu- tion.	Porter's Equa- tion.	Berkeley and Hartley's Equation.	Ideal Equation.	A.	B.	C.	D.
20	15°95 (50° C.)	16°52	—	(50° C.) 20°3	17°9 (0° C.)	—	—
	17°17 (60° C.)	17°19	—	(60° C.) 20°5	—	—	—
	17°74 (70° C.)	17°76	—	(70° C.) 20°68	—	—	—
	17°88 (80° C.)	17°90	—	(80° C.) 20°80	—	—	—
25	24°33 (50° C.)	24°62 (50° C.)	24°62	27°0	24°8 (0° C.)	—	—
	24°27 (60° C.)	24°71 (60° C.)	24°38	27°16	—	—	—
	24°51 (70° C.)	25°07 (70° C.)	24°40	27°30	—	—	—
	24°33 (80° C.)	24°78 (80° C.)	24°39	27°48	—	—	—
45	73°47 (40° C.)	73°26	—	—	69°0 (0° C.)	—	—
	72°03 (50° C.)	72°28	—	—	—	—	—
	73°45 (60° C.)	73°73	—	—	—	72°7 (30° C.)	72°9 (30° C.)
	72°06 (70° C.)	71°95	—	—	—	—	—
60	71°16 (80° C.)	70°58	—	—	—	—	77°0 (57°7° C.)
	150°2 (40° C.)	148°67	—	—	147°5 (0° C.)	—	—
	156°26 (50° C.)	155°11	—	—	—	157 (30° C.)	157°5 (30° C.)
	151°1 (60° C.)	150°48	—	—	—	—	—
	153°37 (70° C.)	149°6	—	—	—	—	160°5 (57°7° C.)
	156°17 (80° C.)	152°64	—	—	—	—	—

Column A.—Morse, "The Osmotic Pressure of Aqueous Solutions" (*Carnegie Institution*, 209.)

" B.—Berkeley and Hartley (*Proc. Roy. Soc.*, 1916, A, 92, 477).

" C.—Frazer and Myrick (*J. Amer. Chem. Soc.*, 1916, 38, 1907).

" D.—Frazer and Lotz (*J. Amer. Chem. Soc.*, 1921, 2501).

### Summary.

1. An improved apparatus for measuring vapour pressure by air bubbling is described, and is shown to give a high order of accuracy over a considerable range of temperatures.

2. The vapour pressures of aqueous sucrose solutions are given over a wide range of concentrations at the following temperatures—40° C., 50° C., 60° C., 65° C., 70° C., 75° C., and 80° C.

3. The densities of aqueous sucrose solutions over the corresponding range of concentrated solutions and temperatures are given.

4. The osmotic pressures of sucrose solutions have been calculated from the vapour pressure measurements by three different methods, and these show good agreement with one another and with the observed values.

*University College,  
Cardiff.*

### DISCUSSION.

*On papers published in VOLUME XXIII., PART I., and read before the  
FARADAY SOCIETY on 26th January, 1927.*

#### The Behaviour of the Quinhydrone Electrode, etc., by J. B. O'Sullivan.

Dr. J. N. Pring said: the quinhydrone electrode is becoming of considerable practical value for the determination of hydrogen ion concentrations in electrolytic solutions such as those employed for the deposi-

tion of different metals, where it is of importance to regulate the acidity. The conclusion to be derived from Mr. O'Sullivan's paper is that hydroquinone which, as is known, is a normal dissociation product of quinhedrone, may exert a reducing action on copper sulphate. I would like to ask if Mr. O'Sullivan has any data relating to this disturbing effect with other metal solutions such as iron, nickel, and chromium.

**The Author** stated that the electrode was useful in acid solutions but, of course, not in the presence of ferric iron.

**The Actinic Absorption of Chlorine Gas with respect to the Hydrogen Chlorine Reaction by W. Taylor; The Residual Effect in the Actinic Absorption of Chlorine by W. Taylor and A. Elliott.**

**Professor Allmand** remarked that, as preliminary experiments made in his laboratory indicated that the quantum efficiency of this reaction did not vary much with frequency in the active visible spectrum region, it seemed possible that the authors' results could be explained in this way, taking into consideration the spectral energy distribution in the light from the Pointolite lamp.

**Mr. A. Elliott:** The source of illumination used in our experiments (100 c.p. "Pointolite" with glass optical system), did not provide radiation of wave-length shorter than about  $350\text{ }\mu\mu$ , so that all the radiation employed was of greater wave-length than that for maximum absorption by the chlorine.

The energy radiated in the ultra-violet ( $\lambda\text{ }350\text{--}400\text{ }\mu\mu$ ) is small compared with that in the region  $\lambda\text{ }500\text{ }\mu\mu$ , but may be more important in promoting activation of the chlorine, owing to the relatively much greater value of the absorption coefficient in the shorter wave region. Quantitative work on this question is at present in progress.

**Vapour Pressure and Heat of Dilution of Aqueous Solutions by W. P. Harrison and E. P. Perman.**

**Professor Donnan** congratulated Professor Perman on his very painstaking and accurate work.

**Professor Allmand** suggested that the inflections in the calcium chloride vapour pressure curves might be connected with the minima in the activity-concentration curves. Application of the Duhem equation showed that the existence of the minimum in the one involved an inflection in the other. Something of the kind appeared to be visible in the vapour pressure data obtained for potassium chloride solutions at  $20^{\circ}\text{C}$ . by Lovelace and Fraser. (*Added subsequent to the meeting.*) On further consideration, it would seem that the authors' methods would not be capable of detecting this inflection unless it were considerably more marked, and that the inflections observed might disappear if vapour pressure were plotted against  $n/N$ .)

He also asked Dr. Perman whether his method would allow of definite measurements being made to within one-tenth of a millimeter.

**Dr. Perman** said the vapour pressures might be considered accurate to  $0.2\text{ mm}$ . He added that he hoped shortly to present a paper discussing the theoretical aspects of the work.

**The Electrostatic Capacity of Aluminium and Tantalum Anode Films by N. A. de Bruyne and R. W. W. Sanderson.**

**Mr. N. A. de Bruyne** in replying to the Chairman's question whether the authors had any physical picture of the surface of a valve anode, replied

that probably the most satisfactory picture was Guntherschulze's, in which the valve action was ascribed to a gas film held in place in the pores of an oxide skin. The law that the capacity of such a film is inversely proportioned to the formation voltage is then equivalent to saying that the thickness of the film grows until a certain minimum potential gradient is attained. They might suppose that the film will grow as long as the anions can pass through and give up their charges to the anode; on this view  $X_0$  was the field of force at the surface of the electrolyte, tending to drag back the anions. Since they were dealing with molecular distances, however, the field of force of the anode (which opposes that of the electrolyte) would also come into play. Thus  $X_0$  would depend on both the metal and the electrolyte or rather the solvent (since this rather than the whole electrolyte would determine the electric field at the surface); measurements of the product Formation Voltage  $\times$  Capacity showed this to be the case. A simple assumption for the rate of growth  $\frac{dx}{dt}$  of the film would be to put  $\frac{dx}{dt} = X - X_0$  where  $X$  is the actual potential gradient at time  $t$ ; since, however,  $X$  is an unknown function of  $x$  the relation cannot be tested.

### REVIEWS OF BOOKS.

**Practical Physics.** By T. G. BEDFORD, M.A., F.Inst.P. (London, 1926: Longmans, Green & Co. Pp. x + 425 with 225 figures. 10s. 6d. net.)

Teachers of physics will be greatly indebted to Mr. Bedford for the care he has taken in writing up the course in practical physics arranged at the Cavendish Laboratory for Part I. of the Natural Sciences Tripos. Taking the book as a whole the standard is about that of a pass degree; but certain essential experiments are missing while others, of quite an elementary character, find a place. Apparently students taking physics at Cambridge start at once on the practical course described in Mr. Bedford's book and, for the benefit of those who have done no practical work at school, a number of very simple experiments are set out in the laboratory. Such experiments include the verification of Boyle's law, the roller and pointer method for linear expansion and the verification of the laws of reflexion of light with pins and a plane mirror. These inclusions would not matter to the general reader if they did not take the place of more important material. Here, however, the omission of any experiments on thick lenses or on the measurement of inductance makes us regret the space devoted to work which really belongs to a more elementary course.

Two aspects of the author's treatment of the subject are particularly good; the excellent judgment he has shown in his selection of theoretical matter and the close attention he has given to experimental technique. The principles underlying the experiments are assumed to be known, but the theory peculiar to each of them is given, except in a few cases where there is good reason for a more extensive treatment. This is no doubt the obvious course to adopt; but the decisions involved are sometimes quite difficult, and practical text-books have been written in which the principles are, on occasion, treated in some detail and the experimental procedure omitted altogether. As for experimental technique the operations to be performed are described to the smallest detail and students using the book will not be able to plead ignorance as an excuse for bad or faulty practice.

The subject is treated under five headings: Mechanics and Properties of Matter, Heat, Light, Sound, Magnetism, and Electricity. The first section in-

cludes experiments on the comparison of masses with the ballistic balance, on moments of inertia, on friction, etc., in addition to those on the subjects always dealt with in a general physics course. The only omission of consequence would appear to be the determination of viscosity by the application of Stoke's formula for falling spheres. This experiment is included in a list of additional exercises at the end of the section, but no student would carry it out properly without detailed instructions. The section on Heat is quite orthodox, although an exercise involving the measurement of temperature with a thermocouple might have been added with advantage. (It is a pity, however, that on p. 105 the author has permitted himself to characterise a thermometer as *delicate*.) Part III. on Light includes, in addition to the usual experiments in geometrical optics, an account of Searle's flare spot method for the refractive index of glass and a number of experiments on interference. The description of the air cell method for finding the refractive index of a liquid by total internal reflection is particularly good. The chapter on Sound is notable for a number of experiments with resonators of various kinds. Part V., on Magnetism and Electricity, includes an unusually large number of experiments with magnets and an account of the theory of the damped ballistic galvanometer, whose application to the measurement of capacity, high resistance, and hysteresis is described.

A little adverse criticism is necessary. The outlook of the book is rather elementary. There are no references (except perhaps half a dozen to Searle's papers and two or three others), and the student receives no special encouragement to read or think about his work. Further, he is not instructed to estimate the errors of his measurements or to assess their influence on the final result. It is true that the introductory chapter discusses the question of the relative accuracy with which the several measurements involved in an experiment should be made, but, unfortunately, most students omit that chapter and, in any case, the matter is one which needs and will bear continual emphasis. In spite of these defects Mr. Bedford has produced the most useful laboratory text-book of its standard available to students in this country. It is obvious that he will have to prepare many future editions, and it is to be hoped that, in the next, he will add twenty or thirty pages dealing with the above-mentioned omissions.

D. O. W.

**Catalysis in Theory and Practice.** By E. K. RIDEAL and H. S. TAYLOR.  
Second Edition. Pp. xv + 516. (London: Macmillan & Co., Ltd., 1926.  
Price 20s. net.)

Seven years have elapsed since the first edition of Rideal and Taylor's monograph on Catalytic Action was published; during that time many new experimental facts on the fundamental processes of catalysis have been brought to light, with the consequence that some of the views of the older generation of physical chemists have been definitely abandoned, whilst others have been drastically modified in order to satisfy the requirements of the recent data. The most arresting outcome of the researches of the past decade is the realisation that (at least so far as actions at solid surfaces are concerned) we are dealing not with the average properties of a crowd of molecules but with the behaviour and functions of a select few—a numerically insignificant proportion—of the total number of atoms which are present in the solid aggregate.

In the present edition this trend of affairs is admirably reflected in Chapters IV., V., and VI., which deal respectively with the theory of heterogeneous catalytic action, promoted and protected catalysts, and poisoning or inhibition of catalytic activity. The many recent investigations relevant to this theory of the

catalytic surface are surveyed thoroughly and critically, with the result that on the whole it is readily seen to what extent our present conception of catalytic action is more or less complete and satisfactory; whilst the treatment given also throws into relief the numerous points which are still not clear and which are either receiving study at the moment in one or other laboratory or are in need of further research. These chapters, and indeed most of the book, go a long way in the direction of realising the authors' hope that the volume will be a further incentive to research and development in this field.

It is perhaps unfortunate that the authors' have not included in the discussion on pages 75-79, a more detailed account of Taylor's theoretical paper<sup>1</sup> in which he has developed a particularly vivid picture of the surface of a nickel catalyst. It may be granted that these pages include this conception in effect, but it is presented with peculiar clarity in the communication in question and in a manner which, in the experience of the writer, is exceptionally readily grasped by the student.

When the present edition is compared with its predecessor, one realises that during the past few years the necessity for consideration of the association of *all* interactants and products with a catalyst has become far better recognised. This is particularly noticeable in catalytic actions into which organic compounds enter, of which class a very complete and readable account is given. Yet the most striking and also one of the earliest proofs of this kind—the formation of a mixture of the *cis*- and *trans*-forms of oleic or elaidic esters when either of the latter individuals are hydrogenated—is not mentioned; that which seems convincing to the organic chemist will probably always not necessarily seem equally important to his physical confrère.

The selectivity of hydrogenation processes is discussed at some length, but the exceedingly delicate susceptibility of such actions to slight modifications in structure, as indicated by the general results of Lebedev, and of other investigators, is not developed fully; quite possibly, however, the communications referred to appeared too late for review in this edition.

Two minor slips which have been noticed may be mentioned here: on page 288 the case of ether formation from diphenyl carbinol in presence of copper at 280° is one of dehydration, not dehydrogenation (as the equation given implies), and on page 302, lines 11 and 12 from bottom should read "transformed cyclohexanol and *methyl cinnamate* by the action of nickel into cyclohexanone and methyl phenylpropionate."

The whole field of catalysis, from both theoretical and practical standpoints, is certainly more completely surveyed in this volume than in any other single work on the subject known to the writer. As is natural (since this edition is only twenty pages longer than the earlier one), the proportion of "theory" has increased at the expense of "practice," so many fresh experimental results having been published in the interim between the two editions. Presumably this tendency will continue for some considerable time and, if the volume is to be kept within its present convenient limits of size, it seems doubtful whether it will continue to be possible adequately to treat both sides of the subject.

Already it is noticeable that the sections on Hydrogen and Hydrogenation Dehydrogenation, and the Fixation of Nitrogen have been shortened considerably, although the technical modifications of these processes continue to be multiplied. The descriptive matter in the concluding chapters of the book, all of which is interesting but much of which deals with reactions of relatively minor importance, might possibly have been sacrificed to some extent in order to set the more important technical phases of catalysis in better perspective.

<sup>1</sup> *Proc. Roy. Soc.* 1925, 108A, 105.

These criticisms are not directed to deprecation in any way of the theoretical discussion of catalysis; indeed, it is to be hoped that the authors will be able in future editions to develop and extend this aspect as the results of fresh researches become available. The writer would like to suggest, in this connection, that that highly important group of catalysts, the natural enzymes, should be still more fully dealt with from the theoretical and experimental standpoint.

The authors have rendered a great service to chemists in collecting together and correlating critically the results of recent work on catalytic action in the two editions of this book; it is to be hoped that they will pursue the same course by similar thorough revision of the volume as opportunity offers. On the whole, they survey the field from a broad and modern standpoint, free from the over-dependence on mathematical symbols and preconceived dogma which marred the outlook of a passing generation of physical chemists. Ostwald's "criteria of catalysis" still act as a kind of ghostly curtain-raiser early in the book—perhaps these may make way for more relevant matter in a subsequent edition?

The members of this Society may ascribe credit to Rideal and Taylor for insisting once again on the priority and clarity of Faraday in this province: "The student of catalysis no less than, for other reasons, the student of electro-chemistry is deeply indebted to Faraday for this early orientation" (1834) "into the mechanism of catalytic action."

The authors are to be congratulated on having produced a volume which is a worthy successor to their first edition; the book is well set up, clearly printed and eminently readable in both senses of the word.

T. P. H.

**Indicators. Their Use in Quantitative Analysis and in the Colorimetric Determination of Hydrogen-Ion Concentration.** By DR. I. M. KOLTHOFF. An authorised translation based on the Second German Edition, revised and enlarged by N. HOWELL FURMAN, Ph.D. (New York: John Wiley & Sons, Inc.; London: Chapman and Hall, Ltd. Pp. 269 + xii. Price 17s. 6d. net.)

The popularity of Dr. Kolthoff's book in its two German editions is ample justification for an edition in English, and it is a happy choice that Dr. Furman should have been asked to undertake the revision and translation of the second German edition. The present work differs considerably from the German issue. A new chapter has been added dealing with amphoteric compounds from the viewpoint of the modern conceptions of Bjerrum; the valuable results of recent investigations of Kolthoff, Michaelis, and others, have been included. Among these additions is a method of preparing a set of buffer mixtures without the use of standard solutions of acid or base.

The measurement of hydrogen-ion concentration has grown to be of such importance, for all branches of chemistry, biochemistry and bacteriology, that the importance of a work such as the present cannot be ignored. It ranks equally with the well-known works of Clarke and Prideaux; in some respects it is of more value than these from the practical point of view. The theoretical aspects receive adequate consideration and modern theories have been applied to the explanation of the action of certain indicators.

The considerable difficulty which is met in the use of indicators for measuring the  $p_H$  of protein solutions makes the use of the electrometric method with the hydrogen electrode a necessity in practice. Although this "protein error" is dealt with in the present work, it is of such practical importance as to warrant fuller consideration.

The only serious error noticed is on page 142, where Sørensen's primary and secondary phosphate buffer should be prepared from 1/15 mol. solutions of both salts and not with 1/10 secondary phosphate as stated. On page 186, in reference 2, the first year given should be 1909 and not 1919.

Taken on the whole, the work is perhaps the best all-round book on the subject we have and should prove of use to those interested in the theoretical side of the measurement of hydrogen-ion concentration, as well as, pre-eminently, to those engaged in its practical measurement. An important feature is the wealth of bibliographical references.

W. C.

**The Corrosion of Metals.** By ULICK R. EVANS, M.A. (London: E. Arnold & Co. Pp. 284. 15s. net.)

The second edition of this book is particularly welcome in view of the rapid development of knowledge in this field. During the last two or three years considerable advances have been made, both in the production and application of materials and, also, as regards a proper understanding of the under-lying principles of corrosion. Although only a short time has elapsed since the publication of the first edition, it is quite clear that considerable effort has been needed on the part of the author to bring the book successfully up to date and to keep it within the relatively small compass intended. Considering the wide interest of the subject, there are relatively few satisfactory books dealing with it. The present volume can safely be recommended to those engaged in works practice who are concerned either with the production or utilisation of corrosion resisting materials, or to those engaged in further research. To the student the book will be found a very complete and reliable guide. In the early pages, the author deals in a useful manner with the electro-chemical aspects of the matter and, also, makes a successful attempt to correlate the numerous facts, many of them apparently small and insignificant, but each having their place in the complete picture necessary for an intelligent appreciation of the problems involved.

Naturally, the author has given considerable space to his own experimental work, but the merit of his researches justifies this, particularly as such work was undertaken in those regions which needed more complete exploration. As regards the metals and alloys now available, it must be conceded that the book contains an adequate account of them; some of the essential outstanding problems of corrosion in the industrial world are ably dealt with.

The author bases his theoretical consideration of the subject largely upon a conception of the mechanism of corrosion based upon electro-chemical phenomena—using “electro-chemistry” in its broadest sense—and upon a study of protective films. Particularly in the latter respect does one feel that he is on right lines and that we are now arriving at some workable theory, which is useful in advancing our knowledge in this field. The chapter on the corrosion of metals in the presence of dissolved oxygen is an outstanding one.

The book is well produced and particularly free from printers' errors.

W. H. H.

# **SECOND EXPERIMENTAL REPORT TO THE ATMOSPHERIC CORROSION RESEARCH COMMITTEE (BRITISH NON-FERROUS METALS RESEARCH ASSOCIATION).**

By W. H. J. VERNON.

*(Received 16th December, 1926, and read before THE FARADAY SOCIETY on 30th March, 1927.)*

## TABLE OF CONTENTS.

	PAGE
INTRODUCTION . . . . .	115
PART I. INDOOR EXPOSURE TESTS AND LABORATORY EXPERIMENTS.	
SECTION I. COPPER.	
A. Introduction . . . . .	117
B. Experimental.	
Atmosphere and specimens employed in normal exposure tests. Method of weighing. Apparatus employed in tests with synthetic atmospheres . . . . .	117
C. Influence of Surface Condition upon Rate of Tarnishing. Effects of Chemical Cleaning.	
Mechanical cleaning. Chemical cleaning; reagents employed in tests, immediate and subsequent effects of treatment . . . . .	119
D. Influence of Purity of the Metal upon Rate of Tarnishing . . . . .	121
E. Influence of Sulphur Content of Atmosphere upon Rate of Tarnishing. Composition of Tarnish Films.	
Determination of, and influence of, "reactive sulphur content" of atmosphere. Determination of sulphide content of tarnish films . . . . .	122
F. Relation between Weight-increment and Time.	
(1) Oxidation at the ordinary temperature, with production of tarnish colours. Theoretical considerations; "short-period" and "long-period" tests; constancy of parabolic relationships under fluctuating atmospheric conditions . . . . .	124
(2) Oxidation at the ordinary temperature without development of colours . . . . .	127
(3) Oxidation at temperatures above normal with development of "temper colours" . . . . .	129
G. Properties of Oxide Films developed in Relatively Pure Atmosphere at the Ordinary Temperature . . . . .	130
H. Properties of Oxide Films developed at Temperatures above Normal . . . . .	130
I. Properties of Sulphide Films.	
The properties of initially-pure sulphide films compared with those of oxide and oxy-sulphide films. The mechanism of tarnishing . . . . .	133
J. Effects produced by "Smoke Films." . . . .	135

## SECTION II. ZINC.

## A. Atmosphere Type 1. "Basement."

- (1) Short-period intensive tests; relation between weight-increment and time . . . . . 135  
 (2) Long-period tests; relation between weight-increment and time . . . . . 137  
 (3) Note upon effect of surface condition . . . . . 138  
 (4) Note upon visual results . . . . . 139  
 (5) Microstructure of surrosion films . . . . . 139

## B. Atmosphere Type 2. "Tank-room."

- Relation between weight-increment and time. Rate of attack as compared with rate of attack in Atmosphere Type 1. Conclusions . . . . . 139

## SECTION III. BRASS.

## A. Relation between Weight-increment and Time.

- Influence of relative humidity; conclusions . . . . . 140

## B. Relation between Intensity of Corrosion and Composition of Alloy 142

## C. Microstructural Changes on Atmospheric Exposure . . . . . 142

## D. Properties of Oxide Films developed at the Ordinary Temperature 142

## E. Properties of Oxide Films developed at Temperatures above Normal 143

## F. Use of Lanoline for protecting Brass exposed to Atmosphere of relatively High Humidity

- Optical and gravimetric results . . . . . 144

## SECTION IV. RELATIVE BEHAVIOUR OF COPPER, ZINC, AND BRASS EXPOSED TO SEVERAL TYPES OF INDOOR ATMOSPHERE.

## A. EXPOSURE IN ATMOSPHERE TYPE 1.

- Varying, but mainly low relative humidity . . . . . 146

## B. EXPOSURE IN ATMOSPHERE TYPE 2.

- Varying, but mainly high relative humidity . . . . . 146

## C. Exposure in Domestic Kitchen.

- Analysis of Corrosion Products . . . . . 146

## SECTION V. ALUMINIUM.

## A. Introduction . . . . . 150

## B. Experimental.

- Atmosphere, specimens, and method of weighing . . . . . 150

## C. Relation between Weight-increment and Time.

- "Short-period" and "long-period" tests; special type of weight-increment curve . . . . . 152

## D. Thickness of Surrosion Film. Influence of Purity of Atmosphere, and of Purity and Physical Condition of Metal . . . . . 154

## SECTION VI. LEAD.

## A. Experimental . . . . . 156

## B. Relation between Weight-increment and Time . . . . . 156

## C. Oxidation Values of Aluminium and Lead compared . . . . . 157

## D. Tarnishing of Lead in Atmosphere contaminated with traces of Vapours from Drying Paint . . . . . 157

## E. Protective Properties of Invisible Oxide Films upon Lead . . . . . 158

## SECTION VII. IRON.

## A. Experimental . . . . . 159

## B. Behaviour in Indoor Atmosphere of Low Relative Humidity, containing Suspended Solid Particles.

- Effect of filtering air and of screening the specimen . . . . . 159

	PAGE
C. Behaviour in Atmosphere Saturated with Water Vapour . . . . .	161
D. Behaviour in Indoor Atmosphere of High Relative Humidity.	
1. The iron is initially free from rust . . . . .	162
2. The iron is initially covered with dry rust . . . . .	162
E. Formation of Invisible Protective Oxide Films.	
Analogy with copper and with lead. Note on passivity . . . . .	164
F. Influence of Purity of Metal upon Rate of Rusting . . . . .	165
G. Behaviour of Iron compared with that of Non-ferrous Materials . . . . .	165

## PART II. OPEN-AIR EXPOSURE TESTS.

INTRODUCTION . . . . .	166
SERIES A. COPPER, ZINC, AND BRASS. 100 WEEKS' EXPOSURE (INTENSIVE TESTS).	
Experimental.	
Specimens employed; method of conducting tests . . . . .	166
DISCUSSION OF RESULTS.	
(1) "Erosion" values.	
Metal attacked and removed in rain. Influence of surface "skin" from manufacture, of physical condition of metal, and of mode of suspension of specimen. Relative erosion of materials; relation between erosion and time. Dezincification of the brasses . . . . .	167
(2) "Surrosion" values.	
Metal attacked but remaining <i>in situ</i> . Computation; analyses of residual corrosion products; dezincification . . . . .	172
(3) Total corrosion.	
Computation; relation between loss in weight and total corrosion . . . . .	174
SERIES B. COPPER (VARIOUS GRADES), ZINC, AND BRASS. 225 WEEKS' EXPOSURE.	
Analysis of residual corrosion products . . . . .	176
Determination of weight-losses, and computation of total corrosion . . . . .	177
Influence of size of specimen . . . . .	178
Relative behaviour of materials.	
(1) <i>Copper</i> .—Influence of modification of composition. Possible connection between loss of reflectivity in early stages, and ultimate resistance to corrosion. Relation between surrosion and total corrosion . . . . .	178
(2) <i>Zinc and Brass</i> . . . . .	178
SUMMARY AND APPENDIX . . . . .	179

## INTRODUCTION.

The 'First Experimental Report' to the Atmospheric Corrosion Research Committee was presented and discussed at a meeting of the Faraday Society on December 17th, 1923.<sup>1</sup> The earlier work was occupied with the systematic examination of the behaviour of the commoner metals on exposure to several types of indoor atmosphere and to the open air, employing both loss of reflectivity and increase in weight to estimate the changes taking place at the metal surface. Probably the outstanding result lay in the recognition of three main types of curve connecting weight-increment with time, the significance of which in relation to the function of the reaction-product was also discussed.

In the work recorded in the present report the examination of the various materials has been carried to a further stage; additional (and

<sup>1</sup> *Trans. Faraday Soc.*, 1924, 19, 839.

generally more intensive) experiments have been instituted. These have been concerned chiefly with the mechanism involved in the formation of various films on exposure to air, with particular reference to the conditions under which protective oxide films may be obtained. To this end, attention has been mainly directed upon copper, partly because of its intrinsic importance and partly because of its special predilection to tarnishing. It was thought that information so gained might be usefully applied to the examination and treatment of the many alloys in which copper is the major constituent. At the same time, zinc and brass have received more critical attention than was the case in the First Report.

A new series of tests upon the metals aluminium and lead has necessitated the recognition of another distinctive type of weight-increment curve.

The experiments upon iron, originally included purely for comparative purposes, have been continued and have brought to light certain factors in the atmospheric corrosion of iron which appear hitherto to have escaped attention.

The arrangement of matter in the present communication differs from that previously adopted. The Discussion on the First Report showed that some confusion had arisen through the use of the term "Field Tests." It was pointed out that in most cases these had been conducted under purely laboratory conditions. In later work the "indoor exposure tests" and "laboratory experiments" have been even more closely identified, and distinction between them has become increasingly difficult. Accordingly, they are now grouped together in Part I. of the Report, whilst Part II. is devoted to the consideration of tests conducted upon specimens exposed freely to the open air. Even in the case of the open-air tests, laboratory methods (for example, optical measurements in the early stages and chemical examination of products both during and after exposure) have been employed, as far as possible, and have enabled definite conclusions to be reached.

In the Introduction to the First Report references to the earlier literature were given and their paucity was commented upon. A list of cognate papers which have been published subsequently is given below, from which it would appear that an increasing amount of attention is being devoted to the behaviour of the non-ferrous metals on exposure to the atmosphere.

- U. R. EVANS. "Relation between tarnishing and corrosion," *Trans. Amer. Electrochem. Soc.*, 1924, **46**, 247.
- G. W. VINAL and G. N. SCHRAMM. "The tarnishing and de-tarnishing of silver," *Met. Ind. (N.Y.)*, 1924, **22**, 15, 110, 151, 231.
- D. H. BANGHAM and J. STAFFORD. "The velocity of oxidation of the metals and the structure of coloured oxide films," *Nature*, 1925, **115**, 83.
- U. R. EVANS. "The colours due to thin films on metals," *Proc. Roy. Soc.*, 1925 (A), **107**, 228.
- U. R. EVANS. "The production of oxide films on copper at the ordinary temperature," *J. Chem. Soc.*, 1925, **127**, 2484.
- E. WILSON. "The electrical conductivity of certain light aluminium alloys and copper conductors as affected by atmospheric exposure," *J. Inst. Elect. Eng.*, 1925, **63**, 1108.
- J. S. DUNN. "The high temperature oxidation of metals," *Proc. Roy. Soc.*, 1926 (A), **111**, 203.
- J. S. DUNN. "The low temperature oxidation of copper," *Proc. Roy. Soc.*, 1926 (A), **111**, 210.
- U. R. EVANS. "Temper colours, tarnish-colours and other tints on metals," *Chem. and Ind.*, 1926, **45**, 211.

W. H. J. VERNON. "The formation of protective oxide films on copper and brass by exposure to air at various temperatures," *J. Chem. Soc.*, 1926, **128**, 2273.

E. WILSON. "The corrosion products and mechanical properties of certain light aluminium alloys as affected by atmospheric exposure," *Proc. Physical Soc.*, 1926, **39**, 15.

## PART I.—INDOOR EXPOSURE TESTS AND LABORATORY EXPERIMENTS.

### SECTION I.—COPPER.

#### (a) Introduction.

In previous work (First Report, *loc. cit.*, 897) the tarnishing of copper under ordinary conditions (*i.e.*, as initiated by traces of sulphur compounds in the atmosphere) appeared to be favoured by a low relative humidity and hindered when the concentration of water vapour was excessively high. The mechanism was concluded to be of a simple chemical character, gas and metal reacting directly and moisture playing a secondary part (*ibid.*, 927). On the other hand, experiments with an atmosphere charged with hydrogen sulphide yielded apparently contrary results, increasing humidity then consistently increasing the rate of attack (*ibid.*, 900). It has since been shown by U. R. Evans, however (*Trans. Amer. Electrochem. Soc.*, 1924, **46**, 265), that *if the concentration of hydrogen sulphide is sufficiently low*, tarnishing is actually hindered by the presence of a film of moisture on the metal surface, a result which brings the two sets of phenomena into agreement.

The present work has shown that although gaseous sulphur impurities may still play an essential part when present in excessively low concentrations, under these circumstances the resulting tarnish film consists mainly of oxide. Examination of the behaviour of films, consisting initially of sulphide, has thrown useful light upon the mechanism of tarnishing in air. The properties of oxide films resistant to tarnishing have also been studied in relation to the conditions under which they may be obtained.

#### (b) Experimental.

*Atmosphere Employed in the Normal Exposure Tests.* In the main series of tests, specimens have been exposed to that indoor atmosphere which was described in the First Report as "Atmosphere Type I. (Basement)" (*loc. cit.*, p. 853). It will be recalled that a pronounced change in hygrometric conditions takes place in May, when the artificial heat supply is cut off from the building and, again, in October when heating is restarted. This is brought out by the following figures; it is noteworthy, however, that the mean temperature alters very little.

	Period S. May-September.	Period W. November-April.
Mean temperature . . . . .	64° F.	67° F.
Mean relative humidity . . . . .	68 per cent.	43 per cent.
Mean daily difference between minimum temperature and dew-point . . . . .	8° F.	22° F.

Under a later heading the influence of gaseous sulphur impurities in very low concentrations is discussed, and a method for their determination is described. For the moment attention is drawn to the numerical results

which are plotted in Fig. 1, representing the variation in "reactive sulphur content" throughout the year. This diagram is comparable with Fig. 1 of the First Report in which the hygrometric values were plotted. As before, a vertical line marks the approximate division between the two periods, but the contrast is now considerably greater. During "Period W" not only is the reactive sulphur content generally high, but the relatively wide limits within which it varies should be especially noted.

*Specimens Employed in the Normal Exposure Tests.* In the tests to be described, the specimens have been taken from high-grade electrolytic copper sheet, 1.2 mm. in thickness. Their dimensions have been either 10.0 × 10.0 cm. as in the earlier tests, or 10.0 × 5.0 cm. in some of the more recent work. The method of abrasion described in the First Report has been relied upon for the preparation of the specimens used in the main series of tests, the final surface having been obtained by means of Hubert No. 1 emery paper as before. For the final cleaning, however, the use of

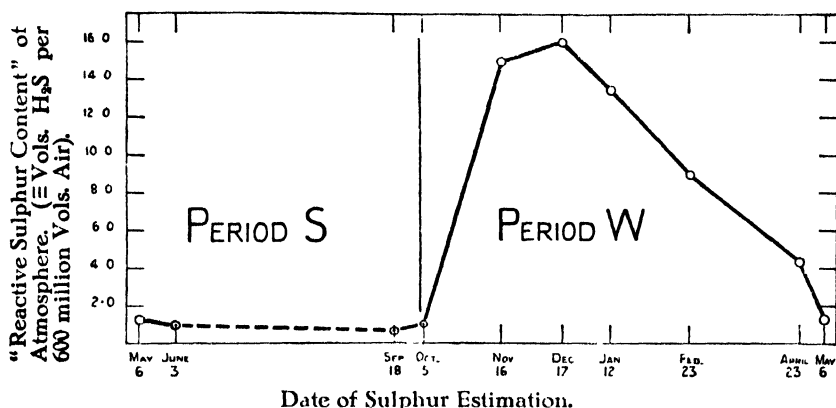


Fig. 1.—Indoor atmosphere employed in tests ("Atmosphere Type I").

Variation in "reactive sulphur content" throughout the year

N.B.—The dotted portion of the curve represents values which are below the limits of satisfactory measurement; they may be regarded, however, as maximum values so far as the actual "reactive sulphur content" is concerned.

organic reagents has been discontinued and dry cleaning with pure cotton wool has been substituted. The method consists in rubbing the specimen repeatedly until no further mark can be obtained upon a piece of the clean wool. Immediately after this treatment the specimens are transferred to a vacuum desiccator and allowed to stand *in vacuo* for weighing and exposure the following day.

*Method of Weighing.* The system of weighing evolved by A. E. Conrady<sup>2</sup> has been followed throughout the work and has proved of the utmost value. A complete weighing includes four partial weighings, each of which in turn involves four readings of the pointer oscillating entirely to one side of the zero. Between partial weighings the specimens and the weights are interchanged. In the course of the present work it has been found advantageous to repeat the whole set of readings with the pointer swinging entirely to the other side of the zero, thus making eight partial weighings as one complete "unit." The method has enabled specimens such as those

<sup>2</sup> *Proc. Roy. Soc.*, 1922, A, 102, 211. The author has enjoyed the advantage of the personal advice of Professor Conrady, whose kindness he gratefully acknowledges.

described above to be weighed consistently correct to 0.01 mg. and, in favourable circumstances, correct to 0.005 mg.

*Apparatus Employed in Tests with Synthetic Atmospheres.* A certain amount of work has already been done with synthetic atmospheres and it is hoped to develop this line of investigation more extensively in the immediate future. The apparatus consists essentially of two desiccators, each of approximately 4300 c.c. capacity, fitted with ground-in stoppers and connecting tube with tap. There are also connections to (i) a purification train through which air can be led, (ii) a small gas-burette from which additions of known amounts of  $H_2S$  or other gas can be made, (iii) a barometer tube and (iv) a vacuum pump. After passing through the purification train the air can be led either through several drying-towers containing phosphorus pentoxide, or through wash-bottles in which it becomes saturated with water vapour, thus enabling any desired humidity to be obtained, the volume of air entering the desiccators being obtained from readings of the barometer tube. One of the desiccators contains the specimens under examination; the other is used as a preliminary mixing chamber for the air. In starting an experiment both desiccators are evacuated and the tap between them is closed. The gases necessary to make up the tarnishing atmosphere are then led into the mixing chamber. After an interval for diffusion the mixture is allowed to divide itself between the two vessels and finally is brought up to atmospheric pressure by the admission of purified air.

### (c) Influence of Surface Condition upon Rate of Tarnishing. Effects of Chemical Cleaning.

*Mechanical Cleaning.* In the First Report it was recorded that surfaces prepared by abrasion with fine emery paper were more susceptible to attack from tarnishing than those in the brightly polished condition; the difference was capable of estimation optically or gravimetrically, although not obvious to visual inspection.<sup>3</sup> The inference that the attack upon emiered surfaces should increase with the coarseness of the emery employed has been confirmed by experiment. Specimens were prepared with fine emery paper (Hubert No. 1) and coarse emery cloth (FF) respectively and were allowed to tarnish under identical conditions. After 36 days' exposure the fine and rough surfaces had increased in weight by 0.93 and 1.42 mg. respectively (the figures are the means of closely agreeing duplicate results); again, however, there was very little to choose between the appearance of the specimens.

*Chemical Cleaning.* Throughout the main tests the method of abrasion has been relied upon for the preparation of specimens, since it was felt that any method of chemical attack would be open to objection on account of the possibility of specific effects due to the reagents employed. Nevertheless, the advisability of obtaining information concerning any such effect has been kept in mind and, to this end, a limited number of experiments have been carried out.

#### *Reagents employed in the Tests, and Immediate Effects of Treatment.*

*Ammonium Chloride, 10 per cent. Solution.* Used boiling, this reagent removes slight stains and very thin oxide films. It has practically no etching effect and no effect on the colour of the copper.

<sup>3</sup> Gravimetric results from "bright" and "dull" specimens after 1300 days' exposure, together with results from comparable zinc specimens, will be found on p. 138.

*Nitric Acid.* (Conc.  $\text{HNO}_3$ , 1 vol;  $\text{H}_2\text{O}$ , 1 vol.) Used cold or warm, this removes relatively thick films of oxide. It etches the metal deeply and, unless the time of treatment is extremely short, leads to severe pitting. Copper cleaned in this way is slightly darker than that cleaned by abrasion alone.

*Nitric-Sulphuric Acid Solution.* (Conc.  $\text{HNO}_3$ , 1 vol; Conc.  $\text{H}_2\text{SO}_4$ , 2 vols.) Of the reagents tried this gives much the best surface to the metal. It does not etch nearly so deeply as the nitric acid alone and does not lead to pitting. Also it has practically no effect upon the colour.

*Chromic Acid Solutions.* (1) Chromic Acid, 20 per cent. aqueous solution. (2) Chromic Acid, 10 per cent.; Ferric sulphate, 5 per cent.<sup>4</sup> (3) Potassium Dichromate, 12 per cent.; Sulphuric Acid, 12 per cent.<sup>5</sup> These solutions, each of which has chromic acid as its effective constituent, are approximately equivalent in respect to their action upon copper. They clean the surface quite thoroughly, but tend to leave a somewhat patchy appearance; moreover, the colour is definitely darker than that yielded by the other methods. The best effect is produced by a previous treatment with the sulphuric-nitric solution, finishing with the chromic mixture (3), whereby "patchiness" is avoided and a slightly paler colour obtained.

#### *Subsequent Effects of Cleaning Treatment.*

Specimens cleaned as above (due precautions being taken to remove all traces of reagent by subsequent washing and drying) were exposed to the basement atmosphere during April, 1926. The results obtained are summarised below.

*Ammonium Chloride Solution.* Visually there is nothing to choose between the behaviour of specimens prepared with emery (Hubert No. 1) only and similar specimens which have also been treated with ammonium chloride solution. Whilst specimens so treated have given slightly greater weight increments, the difference has been too small to justify any significance being attached thereto. This result should be compared with the effects of ammonium chloride upon specimens which have previously been treated with chromate solutions (see below).

*Nitric-Sulphuric Acid Solutions.* Again there is practically no difference in the subsequent behaviour of chemically cleaned specimens and those prepared with fine emery. Moreover, specimens finished by the two methods respectively have given remarkably good agreement in weight-increment.

*Chromic Acid Solutions.* Specimens cleaned with any of the chromic acid solutions have yielded anomalous results, in that they have displayed considerable immunity from tarnishing on subsequent exposure.<sup>6</sup> Thus, after 50 days' exposure the mean weight-increment of such specimens was 0.36 mg. per sq. dm., whereas the mean weight-increment of emiered specimens exposed simultaneously was 0.95 mg. per sq. dm. Whilst these results are not surprising in view of the known passifying action of chromic acid, they are especially significant in connection with results to be described later, where a similar and even more marked protective effect has been obtained by a preliminary heating of the metal in air, with the production of an almost invisible oxide film.

<sup>4</sup> The use of ferric sulphate was suggested by Mr. J. M. Stuart, M.A.

<sup>5</sup> See paper by E. A. Bolton ("The Removal of Red Stains from Brass"), *J. Inst. Metals*, 1925, 33, 143.

<sup>6</sup> It should be noted that Bolton in the work already referred to (*ibid.*, 155) remarks that brass which had been treated with the acid dichromate solution was "resistant to atmospheric tarnishing."

Interest attaches to the effect of following up the chromic acid treatment with immersion in hot ammonium chloride solution. A copper specimen,  $10.0 \times 10.0$  cm., was treated with chromic acid solution (2), washed thoroughly and dried. It was then accurately halved and one portion was immersed for two minutes in boiling ammonium chloride solution (10 per cent.). A similar specimen was cut in two after cleaning with fine emery only, and one half was treated with the ammonium chloride solution. The weight-increments yielded by the four specimens on subsequent exposure to tarnishing conditions for 50 days are given below :—

		Weight-increments. Mgms. per Sq. Dm.
Specimen initially emiered only	(1) No further treatment . . . . .	1.02
	(2) Subsequent treatment with hot ammonium-chloride solution . . . . .	1.10
Specimen initially cleaned with chromic acid solution.	(1) No further treatment . . . . .	0.32
	(2) Subsequent treatment with hot ammonium-chloride solution . . . . .	1.13

It will be seen that, whereas the ammonium chloride solution has had practically no effect upon the emiered specimen, it has entirely destroyed the immunity conferred by the chromic acid treatment. Again, the result is not surprising since the activating effect of ammonium chloride is well-known ; it confirms, however, the existence of an oxide film upon specimens cleaned with chromic acid and, also, shows that, while in the presence of a very thin oxide film the effect of ammonium chloride may be extremely marked, in the absence of such a film it is practically without influence.

#### (d) Influence of Purity of the Metal upon Rate of Tarnishing.

Representative specimens of various grades of copper, including copper containing respectively 0.45 per cent. arsenic, 0.9 per cent. tin, 2.5 per cent. nickel, exposed in the basement atmosphere during period W, have displayed no difference whatever in appearance during the course of tarnishing. (For a description of the visible changes see First Report, *loc. cit.*, 855). The following weight-increments were obtained after a month's exposure :—

	Actual.	Mean.
H.C. Copper . . . . .	$\left\{ \begin{array}{l} 1.96 \\ 1.82 \end{array} \right\}$	1.89 mg. per sq. dm.
Arsenical Copper (0.45 per cent. As) . . . . .	$\left\{ \begin{array}{l} 1.91 \\ 1.85 \end{array} \right\}$	1.88 " " "
Tin Copper (0.9 per cent. Sn) . . . . .	$\left\{ \begin{array}{l} 1.78 \\ 1.70 \end{array} \right\}$	1.74 " " "
Nickel Copper (2.5 per cent. Ni) . . . . .	$\left\{ \begin{array}{l} 1.68 \\ 1.68 \end{array} \right\}$	1.68 " " "

In view of the similarity in appearance it is not surprising that the differences among the mean weight-increments are very small ; nevertheless some definite conclusion can be drawn. Clearly, 0.45 per cent. arsenic has had no measurable influence. The effect of 0.9 per cent. tin is only just appreciable, that of 2.5 per cent. nickel is distinctly more pronounced. In each case the effect is in the direction which would be expected from the ordinary behaviour of the respective elements in the same atmosphere and is of a magnitude commensurate with the proportion present in the copper.<sup>7</sup> It

<sup>7</sup> For example, nickel is unaffected in the present type of atmosphere and it was shown in the First Report (*loc. cit.*, 882) that the rate of tarnishing of copper-nickel alloys is a *function of the copper content*. On the other hand, in a more humid atmosphere copper-nickel alloys undergo a characteristic condensation or "fogging" which is a

may be concluded that the relative purity of the metal, as ordinarily understood, is without any appreciable influence upon the rate of tarnishing.<sup>9</sup>

**(e) Influence of Sulphur Content of Atmosphere upon Rate of Tarnishing. Composition of Tarnish Films.**

*Determination of "Reactive Sulphur Content."* The influence of the relative purity of the atmosphere upon rate of tarnishing was indicated in general terms in the First Report (*loc. cit.*, pp. 897-8). For the purpose of obtaining more exact information a series of tests has since been carried out at representative periods of the year. Each test has consisted in the determination of the "reactive sulphur content" of the atmosphere, whilst at the same time a freshly-cleaned specimen has been exposed and its weight-increment determined after a suitable interval.<sup>9</sup> By "reactive sulphur content" is understood sulphur in such a form that it responds to the "alkaline lead acetate" (sodium plumbite) test. The method actually adopted was as follows. The delivery tube of a Dreschel wash-bottle is drawn out to a jet, leaving a clearance of about  $\frac{1}{8}$  inch between the end of the jet and the bottom of the bottle. A bulb filled with cotton wool is sealed to the outer end of the tube and acts as an air filter. In the bottom of the bottle, immediately under the jet, is fitted a disc of filter paper saturated with alkaline lead acetate solution. Air is drawn through the apparatus at a rate of  $1\frac{1}{2}$  cubic feet per hour and the volume required to produce a faint brown stain upon the paper is noted from an experimental gas-meter in series; this volume is assumed to be inversely proportional to the reactive sulphur content. The test has been calibrated under optimum conditions. Thus, when 10 cub. ft. of air is required to produce the first stain, the reactive sulphur content is equivalent to 1 volume of  $H_2S$  in 35 million volumes of air, a concentration which represents the most intensive tarnishing conditions experienced during the present "normal" tests. Probably the lowest limit of sulphur content to which the method can be satisfactorily employed is about 1 part in 600 million, for the estimation of which the passage of 170 cub. ft. is necessary. Beyond this the incrustation of sodium carbonate seriously interferes with the detection of stain and hence vitiates the result. Fortunately, however, the range indicated above is sufficient for the purpose under discussion. Results of tests covering a period of 12 months are plotted in Fig. 1.

*Influence of "Reactive Sulphur Content."*—The results of a series of sulphur determinations, together with corresponding tarnishing results, over a period including the maximum and minimum values referred to above, are set out in Table I. It may be noted at this point that during the months of July, August, and September (represented by a dotted line in Fig. 1) tarnishing ceases, *i.e.*, the metal no longer passes through any colour changes. As to the corresponding reactive sulphur content all that can be said at present is that it is less than 1 volume in 600 million, the lowest limit of estimation with the method described above.

function of the nickel content. It is significant that after exposure to the atmosphere of the "tank room" (*loc. cit.*, 853) for a sufficient time the weight-increment of copper containing  $2\frac{1}{2}$  per cent. nickel is appreciably higher than that of the pure metal.

<sup>9</sup> This is in striking contrast with the conclusion reached in connection with the *open-air corrosion* of copper (see Part 2), where 0.45 per cent. arsenic is shown to have a profound influence in reducing the total loss by corrosion.

<sup>9</sup> This procedure is justified by results described under the next heading which show that the rate of attack upon the metal, even after comparatively long periods, is determined very largely by the conditions prevailing at the time of the first exposure.

From the results in Table I. (see second and last columns) the interesting result emerges that if the rate of tarnishing be taken as proportional to the *square* of weight-increment per unit time<sup>10</sup> then *rate of tarnishing is directly proportional to the reactive sulphur content of the atmosphere.*

TABLE I.

RELATION BETWEEN REACTIVE SULPHUR CONTENT OF ATMOSPHERE AND RATE OF TARNISHING OF COPPER.

Date.	Atmosphere.		Specimen : Rate of Tarnishing.	
	Volume of Air Taken to Produce Stain (Cub. Ft.).	Reactive Sulphur Content (Vols. H <sub>2</sub> S Per 600 Million Vols. Air).	Actual (Mg. per Sq. Dm. per Day) <sup>2</sup> .	Relative.
1925.				
Dec. 17 .	11	16.0	0.177	16.5
1926				
Jan. 12 .	13	13.5	0.165	15.4
Feb. 23 .	20	9.0	0.118	11.0
Apr. 23 .	40	4.4	0.042	3.95
May 6 .	135	1.3	0.015	1.4
June 3 .	175	1.0	0.0107	1.0

*Composition of Tarnish Films.* The fact that the rate of tarnishing is directly proportional to the reactive sulphur content of the atmosphere renders it particularly expedient to enquire into the sulphur content of the resulting tarnish film.<sup>11</sup>

Copper specimens were exposed on Nov. 21st, 1923, and allowed to tarnish in the usual way. On July 16th, 1925, the weight increment was 5.4 mg. per sq. dm. and determinations showed that of this increment 0.58 mg. was due to sulphur, *as sulphide*, *i.e.* 10.7 per cent. On Sept. 10th, 1926, the weight-increment was 6.1 mg. per sq. dm., of which 0.61 mg. was due to sulphur, *i.e.* 10.0 per cent.

Other specimens were exposed on Dec. 19, 1925, and on Sept. 9th, 1926, the weight-increment was 2.6 mg. per sq. dm., of which 0.4 mg., or 15.7 per cent. was due to sulphur, again as sulphide.

These results show clearly that instead of the film consisting essentially of sulphide as was thought in the early days of the work, sulphide enters only to a minor degree into its composition. It is true of course that it is an *essential constituent*, and the proportions found by experiment are certainly more in accord with the concentration of atmospheric sulphur upon which the tarnishing process depends. Nevertheless it is remarkable that such excessively small traces of sulphur in the atmosphere can determine the oxidation of the metal at the ordinary temperature to such relatively gross extents.

It may be noted that the foregoing results throw considerable light upon

<sup>10</sup> A little consideration will show that this is actually a sound method of computing the rate of attack, where a *parabolic* relationship obtains between weight-increment and time.

<sup>11</sup> The method ultimately employed for the estimation of the very small amounts of sulphur is stated in the Appendix. For the particular purpose of these experiments, specimens in the form of foil were employed, as distinct from the thin plates used in the bulk of the tests.



which is quite typical of the results obtained, it will be seen that the early part is *very nearly a straight line*. The squares of the weight-increments show that from a certain point onwards ("P" in Fig. 2) the curve is accurately parabolic and, moreover, the position of this point, marking the transition from the straight line to the parabola, is fairly sharply defined.

A simple explanation of this state of affairs is readily forthcoming and is doubtless connected with the fact already noted that in the case of a flat specimen the attack does not begin at all parts of the surface simultaneously, but proceeds from the *edges inwards*. Clearly, the method of calculating

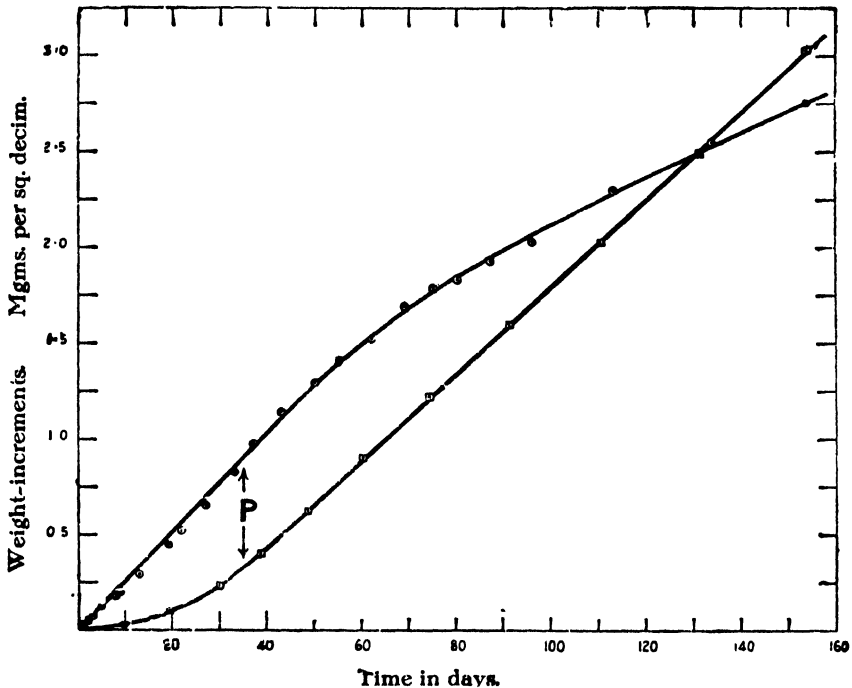


Fig. 2.—Oxidation (tarnishing) of copper at ordinary temperature in atmosphere containing traces of sulphur compounds. (See Fig. 1, Period W). Square specimens. Relation between weight-increment and time in the very early stages.

□ = Squares of weight-increments (values taken from smooth curve)  $\times 0.4$ .

the actual weight-increment upon the total area cannot be expected to yield a parabola during the period when only a portion of this area is actually undergoing attack. The matter is rendered clearer if it be remembered that equation (1), as it stands, is only true for a surface the whole of which is being simultaneously attacked, unless indeed it is regarded as representing only a small element of the surface. Otherwise it should be written

$$\left(\frac{W}{A}\right)^2 = Qt. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $A$  is the actual area which has suffered the change represented by the increase of weight  $W$ , at any particular time  $t$ . But in the example



exposure of 1300 days—were obtained from the identical specimens whose weight-increments up to 114 days formed the subject of Fig. 8 of the First Report. It is important to note that in each of the four years represented in Fig. 3, the atmosphere has passed through the changes in type which have already been discussed, giving rise to two periods in each year ('W' and 'S' respectively) the approximate durations of which are indicated by vertical lines in the diagram. From the squares of the weight-increments it will be seen that the parabolic relationship has been followed very closely for the whole time, in spite of the fluctuations in external conditions.<sup>13</sup> When it is recalled how profoundly different are the intrinsic effects upon copper during the winter and summer periods, respectively, the significance of this result will be appreciated. One is indeed led to the conclusion that the *rate of attack is determined by the conditions prevailing at the time of the first exposure* and that external conditions may subsequently vary within extremely wide limits without disturbing the course of the attack. The important corollary follows that the process must be very largely controlled by the properties of the initially-formed film.

#### **Relation between Weight-Increment and Time—(2). Oxidation at the Ordinary Temperature without Development of Colours.**

It has already been mentioned that during the summer period, when the concentration of atmospheric sulphur falls below a certain excessively small limit, copper specimens cease to undergo any appreciable visible change on exposure. Nevertheless the formation of a film of sufficient thickness to confer protection upon the underlying metal is demonstrated by the fact that, on emerging into the winter period, such specimens *still retain their immunity from tarnishing whilst freshly-cleaned specimens tarnish in the usual way*. Arising from this observation the attempt was made to trace the development of the protective film gravimetrically; the results of a typical series of weighings are plotted in Fig. 4. The experiment was started and most of the weighings conducted during Period S; the last point on the curve, however, falls well within Period W. To facilitate comparison the early part of the curve (Fig. 2) previously discussed as typical of Period W, is plotted on the same diagram, to the same scale and in its correct chronological position. Apart from the great disparity in the respective rates of attack, interest chiefly attaches to the disposition of the curves in the early stages. It is significant that in the case of exposure during the summer period the curve is parabolic from the start, as distinct from the straight line which characterises the early part of the other curve, the meaning of which has already been discussed. From similar considerations it follows that in the present instance the initial attack takes place simultaneously over the whole surface.<sup>14</sup>

One additional and important point remains to be noted. It will be observed that the curve which started in period S is undeflected from its original course on emerging into period W, notwithstanding the excessive increase in the activity of the atmosphere. Thus, of the two alternatives presented, the continuance of the type of film already started is preferred

<sup>13</sup> Results up to 1600 days will be found in Fig. 12.

<sup>14</sup> It is for this reason that it is still possible to measure the weight-increment after the first day's exposure, notwithstanding that the intrinsic rate of attack is so very much less; indeed, in the examples plotted, the value for one day's exposure was actually greater for curve S than for curve W.

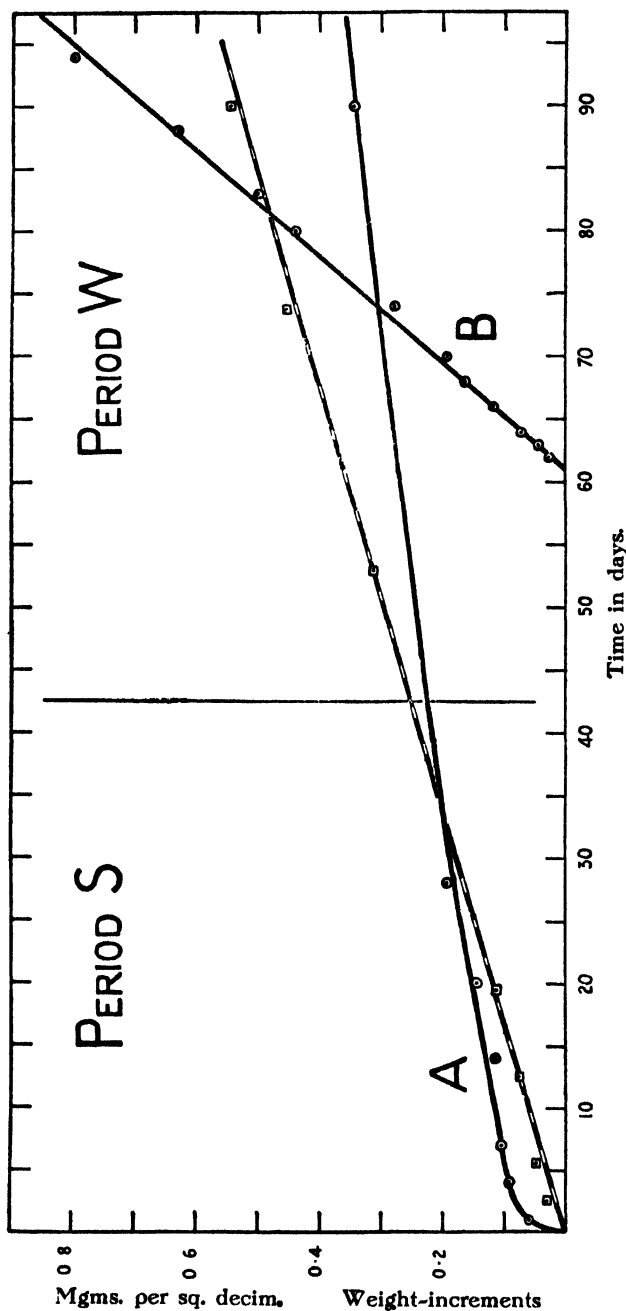


Fig. 4.—Period S (Curve A).—Oxidation of copper at ordinary temperature in relatively pure atmosphere. Relation between weight-increment and time.

[□] = Squares of weight-increments (values taken from smooth curve) × 5.0

Period W.—Attack upon, freshly-cleaned copper (Curve B). Immunity of copper protected by thin film of oxide. (Continuation of Curve A).

to the building up of an entirely different type, in spite of the apparently greater inducement in favour of the latter course. This example appears to provide even more striking confirmation of the principle which has

already been enunciated (from consideration of curves started in period W), that the rate of attack is largely determined by the conditions prevailing at the time of the first exposure.

### Relation between Weight-Increment and Time—(3). Oxidation at Temperatures above Normal, with Development of "Temper Colours."

The phenomenon of "temper colours," *i.e.* the characteristic sequence of colours developed during the heating of metals at suitable temperatures in air, is clearly sufficiently cognate to warrant some measure of attention in an enquiry of the present kind. Between these colours and the tarnish colours produced at normal temperatures there is sufficient general resemblance to suggest at once a similar physical cause, *i.e.* the interference of light in the film of reaction product. From previous considerations,

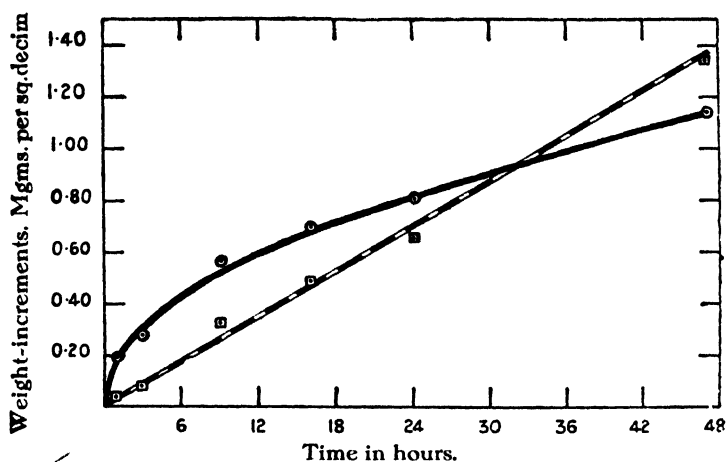


Fig. 5.—Oxidation of copper at 150°C. (with development of "temper colours"). Relation between weight-increment and time.

— = Squares of observed weight-increments.

therefore, a parabolic relationship between thickness of film and period of exposure at any given temperature would again be expected and, since complications due to any "edge effect" are now absent (*i.e.* the colours associated with any particular combination of temperature and time are exhibited uniformly over the surface) the weight-increment/time curve should be parabolic from the start. To put this reasoning to experimental test a series of determinations was carried out at 150°C., the results of which are plotted in Fig. 5.<sup>15</sup> The times of heating varied from one hour, giving a bluish-purple film, to 47 hours when a dull reddish-brown film (a second order colour) was obtained. From the squares of the weight-increments it will be seen that the foregoing considerations are satisfactorily borne out. The absence of any initial straight line suggests at once that

<sup>15</sup> Attention should be called to a recent paper by J. S. Dunn (*Proc. Roy. Soc.*, 1926, A., III, 210). By noting the sequence of temper colours on copper heated in air, and plotting "equivalent air thickness" against time, Dunn obtained well-defined parabolas for temperatures between 184° and 444° C. At the latter temperature the parabolic relationship was confirmed by measuring the fall in electrical conductivity.

traces of sulphur compounds do not play the essential part which they do in tarnishing; experiments have confirmed that within the limits which have already been discussed (see Fig. 1) relative purity of the atmosphere is practically without influence in the development of temper colours.

**(g) Properties of Oxide Films Developed in Relatively Pure Atmosphere at Ordinary Temperature.**

The evidence described under previous headings leads to the conclusion that the film which develops upon copper at the ordinary temperature in an atmosphere of relatively high purity is totally different in properties from that which forms, also at ordinary temperature, in the presence of traces of sulphur compounds. In contradistinction to the latter, the former shows no interference colours; it is not only independent of the presence of traces of sulphur compounds in its formation, but when once formed, it is relatively impervious to their presence.

It seems reasonable to believe that the explanation lies in a fundamental difference in the original space lattice of the two types of film respectively. Thus, it can readily be imagined that the one in which sulphur does not appear will resist the intrusion of sulphur atoms into the lattice and, hence, will protect the underlying metal. On the other hand, when the clean metal surface is exposed to an atmosphere containing traces of sulphur, it is probable that sulphur atoms take an essential part in the formation of the first lattice, which is therefore of such a type as to permit of the diffusion of more sulphur atoms to the underlying metal; hence the building up of the same lattice is facilitated.

The imperviousness of the sulphur-free oxide film is clearly a matter of importance in view of the protection afforded to the underlying metal. The protective effect is shown graphically in Fig. 4; it may also be illustrated by the following figures. Specimens exposed for a month during period W increased in weight by 0.8 mg. per sq. dm. During the same time specimens which had been previously exposed for a month during period S increased by 0.06 mg. per sq. dm.; moreover, during their *whole period* of exposure they had increased by only 0.3 mg. per sq. dm. without, it may be added, the accompaniment of any colour changes.

**(h) The Properties of Oxide Films Developed at Temperatures above Normal.**

The protective character of the film obtained by exposing copper to a relatively pure atmosphere at the ordinary temperature suggests at once that a similar degree of protection might be conferred more rapidly by exposure at higher temperatures. Actually it was found in 1923 that very similar effects could be obtained in as short a time as 1 hour by simply raising the temperature to 100° C. Furthermore, the formation of the (almost invisible) protective film at 100° C. was found to be independent of the time of year at which the treatment was conducted and no special purification of the air was necessitated. It was felt desirable, however, to carry the matter to a further stage and investigate the effects produced by heating specimens at both lower and higher temperatures.

The results of this enquiry have formed the subject of a separate paper.<sup>16</sup> Specimens were heated for 1 hour at temperatures extending from 50° to

<sup>16</sup> W. H. J. Vernon, *J. Chem. Soc.*, 1926, 128, 2273.

250° C.; below 100° the films obtained were practically invisible, but at higher temperatures the usual sequence of interference colours was observed. Weight-increments were determined, and their relationship with temperature was found to conform exactly to an equation developed by J. S. Dunn,<sup>17</sup> but previously verified for much higher temperatures only. This equation is identical in form with the Van't Hoff isochore, *i.e.*—

$$d \log W/dT = - Q/RT^2.$$

The agreement will be seen by reference to Fig. 6 where logarithms of weight-increment are plotted against reciprocals of absolute temperature.

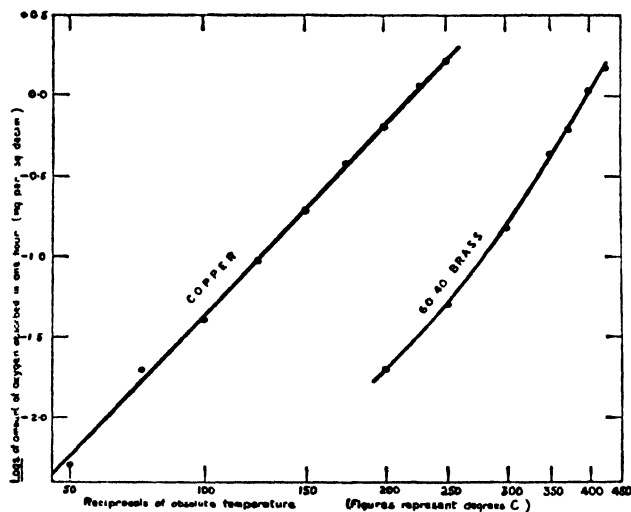


Fig. 6.—Influence of temperature on rate of direct oxidation (Copper, and 60/40 brass).

Subsequent exposure of heat-treated specimens during Period W yielded results of particular interest, as will be seen from the following description of the visible effects after 20 days' exposure:—

- |                           |   |
|---------------------------|---|
| 1. Unheated specimen      | . Tarnished a reddish-purple colour.  |
| 2. Heated at 50°          | . Reddish-purple (exactly as 1).  |
| (similarly for 55°)       | . No change since heat-treatment, <i>i.e.</i> practically unaltered copper.   |
| 3. Heated at 75°          | . No change since heat-treatment, <i>i.e.</i> slightly darker than 3, as result of heat-treatment, but otherwise unaltered. |
| 4. Heated at 100°         | . No change since heat-treatment, <i>i.e.</i> series of interference colours ( <i>loc. cit.</i> ).                          |
| 5.-10. Heated at 125-250° |   |

Considerable significance attaches to the fact that an hour's heating in air at a temperature as low as 75°—a treatment practically without any visible effect upon the metal—is sufficient entirely to inhibit the development of interference colours on subsequent exposure to tarnishing conditions. The conclusion is inevitable that the protection is brought about by a film of oxide, either so thin as to be almost invisible (as by heating at 75°), or, while still transparent, sufficiently thick to refract light (as by heating at temperatures above 100°).

<sup>17</sup> *Proc. Roy. Soc.*, 1926, A., III, 203.

The very sudden break in the behaviour of specimens heated at  $55^{\circ}$  and  $75^{\circ}$  respectively, suggested that a film of minimum thickness was necessary for protection, and an explanation was attempted based on the estimated thickness of the film. Assuming the first product of interaction of copper and oxygen to be cuprous oxide (density 6.0), and taking from Fig. 6 the weight of oxygen absorbed, the figure obtained for the thickness of the film produced at  $55^{\circ}$  was 10.5 Ångstrom units. In the calculation the nominal area of the specimen was assumed, but if a value more nearly approaching the true area had been employed (bearing in mind the emiered nature of the surface), undoubtedly the result would have approximated much more closely to the value usually accepted for the lattice dimensions of cuprous oxide, *i.e.*, 4.3 Å. u. The suggestion was made therefore that *the minimum thickness of film necessary for protection may be such that the unit lattice of the oxide is completed for the whole of the surface.*

TABLE II.

COPPER : WEIGHT-INCREMENTS SUBSEQUENT TO HEAT-TREATMENT.

Temperature of Heating, °C.	Period of Exposure, and Increase in Weight (mg. per sq. dm.).				
	Series A.			Series B.	Series C.
	6 Days.	34 Days.	100 Days.	152 Days.	206 Days.
(Not heated)	0.29	0.91	1.28	1.68	2.60
50	0.21	0.76	1.12	—	—
75	0.00	0.30	0.42	—	—
100	0.00	0.17	0.31	0.40	0.43
125	0.00	0.11	0.28	0.39	—
150	0.00	0.15	0.24	0.34	—
175	—	—	—	0.32	—
200	0.00	0.12	0.22	0.34	—
225	—	—	—	0.32	—
250	0.00	0.19	0.26	0.33	—

Weight-increments (subsequent to heat-treatment) of the specimens discussed above are given in Table II. (Series A) and are plotted in Fig. 7. Gravimetric data for other (less complete) series after longer exposure are also included in Table II. Although protected specimens slowly increase in weight, they do not appear to undergo any further colour change. Actually the gravimetric method does not give a satisfactory response to visible changes, and the measurement of loss of reflectivity as employed in the earlier work (First Report, *loc. cit.*, 851) is in this respect much to be preferred.

The results recorded above were obtained with specimens that had been polished with fine emery paper (Hubert No. 1). Tests conducted upon a limited number of specimens brightly polished with mechanically driven "mops" yielded results which, although quite convincing gravimetrically (the figures comparing favourably with those given in Table II.), were not so satisfactory from the point of view of the suppression of visible changes. In these tests, however, no other temperature than  $100^{\circ}$  was employed for the heat-treatment and further work seems to be necessary in the case of copper polished in this way.

## (i) Properties of Sulphide Films.

In view of the characteristic properties of oxide films and of "oxy-sulphide" films which have been discussed above, interest attaches to the behaviour of films consisting initially of pure sulphide on exposure to the atmosphere. To obtain comparable information upon this point specimens of copper foil, each measuring 10.0 cm.  $\times$  5.0 cm. were cleaned in the usual way and submitted to initial treatment as follows:—

A. Heated in air at 150° C. for 20 minutes. The thickness of the resulting oxide film was such as to give an orange "temper colour," corresponding with that obtained by heating for one hour at 125°. (See

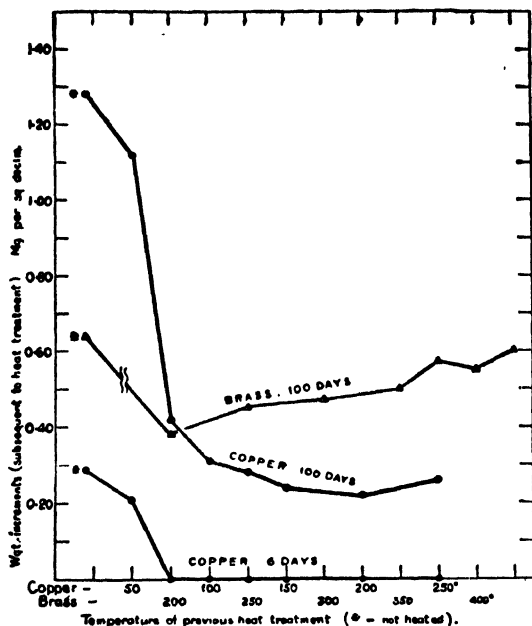


Fig. 7.—Weight-increments due to oxidation (tarnishing) of copper and 60/40 brass at the ordinary temperature, in relation to temperature of previous heat-treatment (for one hour).

Fig. 6.) Increase in weight = 0.10 mg. per sq. dm. (very nearly). Approximate film thickness = 150 Å. u.

B. Heated in air at 150° for one hour. "Temper colour" = fine rose. Increase in weight = 0.20 mg. per sq. dm. (very nearly). Approximate film thickness = 300 Å. u.

C. Exposed to atmosphere of hydrogen sulphide for short period until an orange interference colour, practically identical in appearance with A, was obtained. Then submitted to vacuum desiccation several times in order to remove any associated hydrogen sulphide. Increase in weight = 0.10 mg. per sq. dm.

D. Exposed to similar atmosphere of hydrogen sulphide for a longer period until the almost exact colour equivalent of B was obtained, i.e. "rose"; then vacuum desiccation as before. Increase in weight = 0.25 mg. per sq. dm.

E and F. No initial treatment other than cleaning.

Besides the untreated "blanks," the specimens thus included two typical oxide films (one twice the thickness of the other) together with two corresponding sulphide films; after preparation as above the whole were exposed to the basement atmosphere during "period W." Interesting visual results quickly followed. In striking contrast with the heat-treated specimens, which showed no sign of change,<sup>18</sup> those initially covered with sulphide proceeded (at of course a modified rate) *through the same succession of colour changes which they would have done if the treatment with hydrogen sulphide had been continued.* In two days the "thin" sulphide film had progressed to the stage initially represented by the "thick" film, *i.e.* a "rose" colour, whilst the thick film was then deep blue; in three days the colours were purple and steely blue respectively. The rate of change of specimens initially covered with sulphide was visibly greater than those exposed in the freshly-cleaned condition; thus, in three days the "blanks" had not progressed beyond a deep orange border.

After one month's exposure the specimens were weighed and the sulphur (sulphide) content of the films was determined.

TABLE III.

BEHAVIOUR OF SULPHIDE AND OXIDE FILMS ON EXPOSURE TO THE ATMOSPHERE.

	Nature of Initial Film.	Weight of Oxygen or of Sulphur in Initial Film. Mg. per Sq. Dm.	Weight-Increment Subsequent to Exposure. Mg. per Sq. Dm.	Weight of Sulphur Absorbed Subsequent to Exposure. Mg. per Sq. Dm.	Proportion of Subsequent Weight Increment Accounted for by Sulphur.
A	Oxide	0.10	0.25 }	< 0.002 <sup>19</sup>	< 1.0 per cent. <sup>19</sup>
B	"	0.20	0.18 }		
C	Sulphide	0.10	1.64	0.45 }	26.2 "
D	"	0.25	1.71	0.43 }	
E	"Blank"	—	1.06	0.19 }	14.8 "
F	"	—	1.11	0.13 }	

In Table III. the increases in weight subsequent to the initial treatment are given, together with the corresponding increment in sulphur content; in the last column the proportion of sulphur which is responsible for the subsequent weight-increment is expressed as a percentage of that increment. It will be seen that the presence of the initial sulphide film has not only caused a definitely greater attack upon the underlying metal, but also it has materially increased the selective absorption of sulphur from the atmosphere. On the other hand the powerful restraining influence of the initial oxide film is confirmed; moreover, the figures quoted for sulphur content demonstrate the virtual impenetrability of this film by ordinary atmospheric sulphur.

Incorporating what appear to be reasonable conclusions with statements of fact, the position may be summed up as follows. Films of pure oxide upon copper are relatively impervious to oxygen atoms at the ordinary temperature and excessively impervious to sulphur atoms. Pure sulphide

<sup>18</sup> Similar heat-treated specimens have now been exposed for 12 months and have as yet showed no visible alteration.

<sup>19</sup> These values were obtained from examination of similar heat-treated specimens which had been exposed for nearly 12 months.

films, on the other hand, are relatively pervious both to oxygen and sulphur atoms; moreover, compared with a freshly cleaned copper surface, they favour the selective absorption of sulphur. Exposed to an ordinary atmosphere containing traces of sulphur as impurity, sulphide films increase in thickness mainly through absorption of oxygen; the optical homogeneity of the film is maintained however (*i.e.* there is no break in the sequence of interference colours), which leads to the suggestion that isomorphous mixtures of sulphide and oxide are produced. In the case of clean copper surfaces exposed to a similar atmosphere, films of this isomorphous type are produced at the outset; these films contain a preponderance of oxide over sulphide, but their permeability is excessively greater than that of the pure oxide and is not far removed from that of the pure sulphide. The function of traces of atmospheric sulphur in this respect appears to be akin to, if not identical with, that of catalysis; the conclusion is reached that it is the "activation" of the first oxide lattice through the impingement of sulphur atoms which entirely determines the subsequent course of attack.

### (j) Effects produced by "Smoke Films."

In the course of the present work some experiments were carried out by Mr. L. Whitby some time ago with the object of ascertaining the effect of smoke (particularly tobacco smoke) upon a clean copper surface.

Specimens prepared in the usual way were placed in tubes, which were then filled with smoke, and sealed. Contact with the smoke produced very little visible effect upon the metal, and hence a negative result was recorded. Later, however, the surprising fact was noted that specimens which had received this treatment still retained their practically unaltered appearance when exposed to conditions such that untreated specimens tarnished rapidly. It was found that immunity from tarnishing was conferred by exposure to tobacco smoke and the smoke from cellulose, either in the form of pure cotton wool or in the less pure form of paper or rag.<sup>20</sup> The best results, however, were obtained from the pure cellulose smoke, since this had the least visible effect upon the metal in the first place, whilst yielding equally good results on subsequent exposure. Similar protective effects were observed upon silver (both "fine" and "sterling") as the result of this treatment; the actual extent of the protection can be gauged from the fact that the attack of an atmosphere highly charged with hydrogen sulphide (in which the untreated metal became severely tarnished in a few minutes) was resisted for as long as 24 hours. The phenomenon is one which would probably repay further study, but for the present it is merely recorded as an interesting observation.

## SECTION II.—ZINC.

### A. ATMOSPHERE TYPE 1.—BASEMENT.<sup>4</sup>

#### (i) Short-period (Intensive) Tests: Relation between Weight-Increment and Time.

In previous work the relationship between weight-increment and time in the case of zinc exposed to the "unsaturated" type of atmosphere was shown to be consistently linear (First Report, *loc. cit.*, 863). Although,

<sup>20</sup> The smoke from wool, however, so far from protecting, has an intrinsic and considerable tarnishing effect, due of course to the sulphur content of the wool.

<sup>21</sup> For description see First Report, *loc. cit.*, 853, and the present report, p. 117.

as in the experiments with copper, the first point plotted was always at an appreciable distance from the origin, the results left little room for doubt that this relationship actually held from the start. Nevertheless it was felt

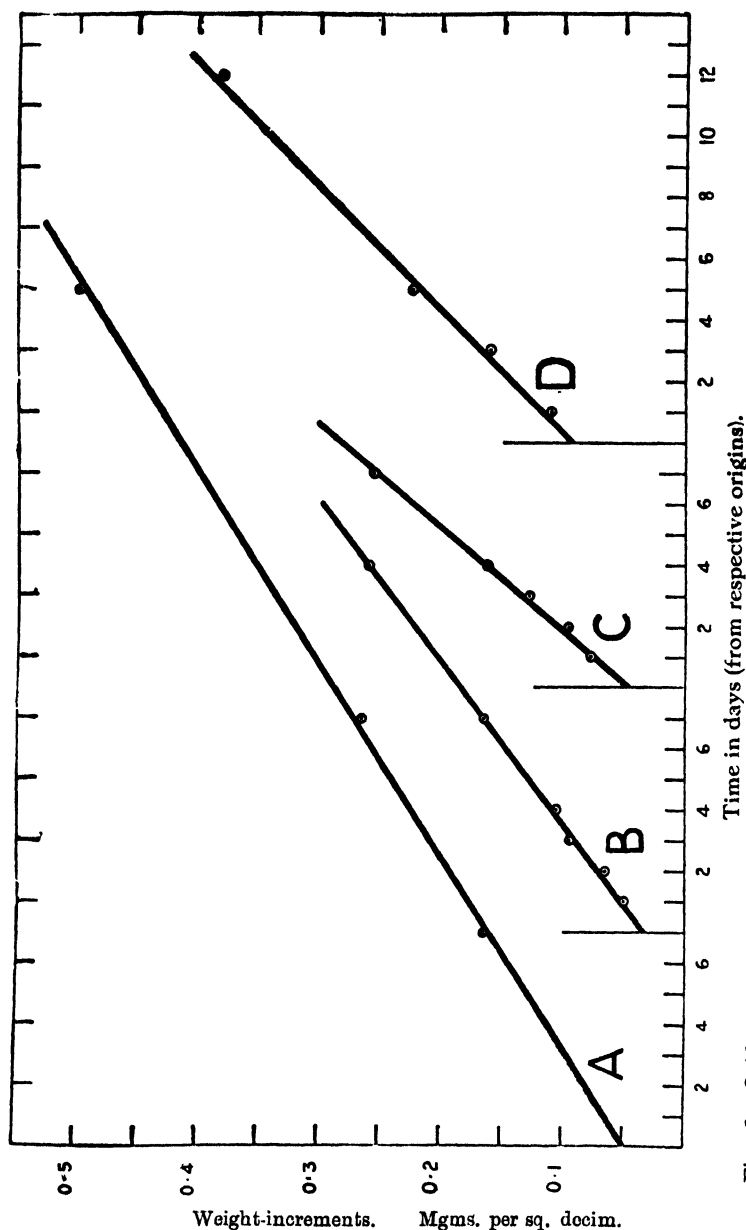


Fig. 8—Oxidation of zinc at the ordinary temperature. Relation between weight-increment and time in the very early stages.  
Dates of Starting.—A, Jan. 29; B, April 24; C, May 12; D, Aug. 19 (1925).

expedient to include among the more recent work a limited number of tests upon zinc, employing similar intensive methods as for copper. Each specimen measured  $10.0 \text{ c.} \times 10.0 \text{ cm.}$ , and was prepared in the usual manner (see p. 118).

Results obtained from tests started on four separate occasions are represented in Fig. 8; the figures plotted are the means of closely-agreeing duplicates and with one exception include the weight-increment from the first day's exposure onwards. Two interesting features will be noted: (1) from the first day the points fall with striking precision upon a straight line, thus confirming the linear relationship for very short exposure which was the main object of the tests; (2) the straight line does not quite pass through the origin, but cuts the vertical axis, indicating a greater initial rate of attack, which quickly assumes a lower and constant value.

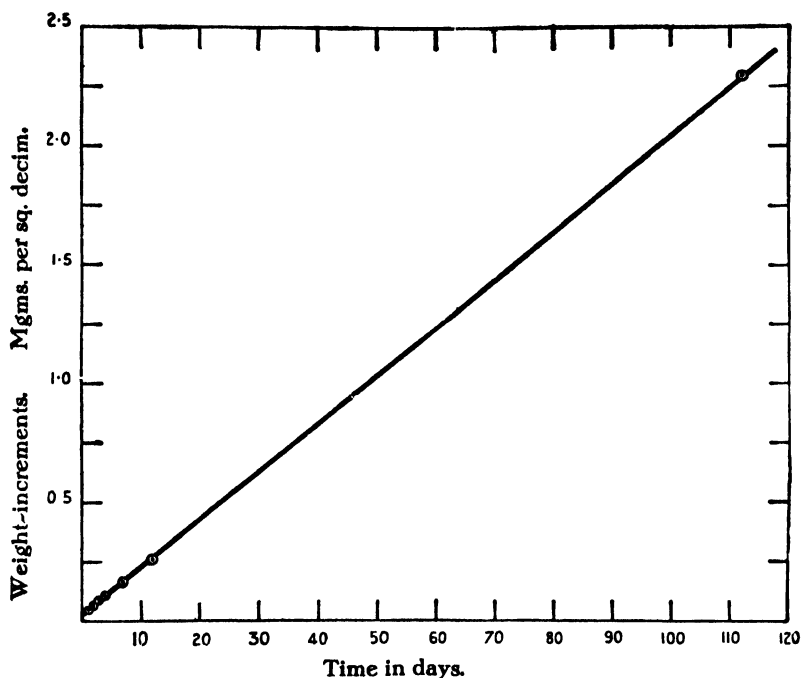


Fig. 9.—Oxidation of zinc at the ordinary temperature. Relation between weight-increment and time. "Short Period." (Continuation of Curve B, Fig. 8).

The very open scale upon which Fig. 8 is plotted should be borne in mind. After longer periods of exposure the discrepancy at the origin becomes relatively smaller and therefore difficult to detect on a close-scale diagram. Thus, in the case of curve B the last point plotted was at 12 days; no further determinations were made until 112 days, and the results at that stage are shown in Fig. 9. It will be noted how exactly the original straight line has persisted and, also, how insignificant the original deflection from the origin now appears; clearly, after more prolonged exposure a "fair curve" through the points would fail to distinguish it at all.

## (2) Long-period Tests. Relation between Weight-Increment and Time.

From the intensive short-period tests described above it is of interest to turn to the other extreme and consider the behaviour of zinc exposed

during the longest periods over which records are available. That the linear relationship is still maintained will be seen by reference to Fig. 10, where results extending over a period of  $3\frac{1}{2}$  years are plotted. Considering the neutral or perversive character of the scale it may appear surprising that the seasonal fluctuations in atmospheric conditions (see p. 117) have not affected the long-period tests to a greater extent. The explanation lies in the fact not only that the room temperature is fairly equable throughout the year, but also that variations in relative humidity and in "reactive sulphur content," within the limits already described, have little if any

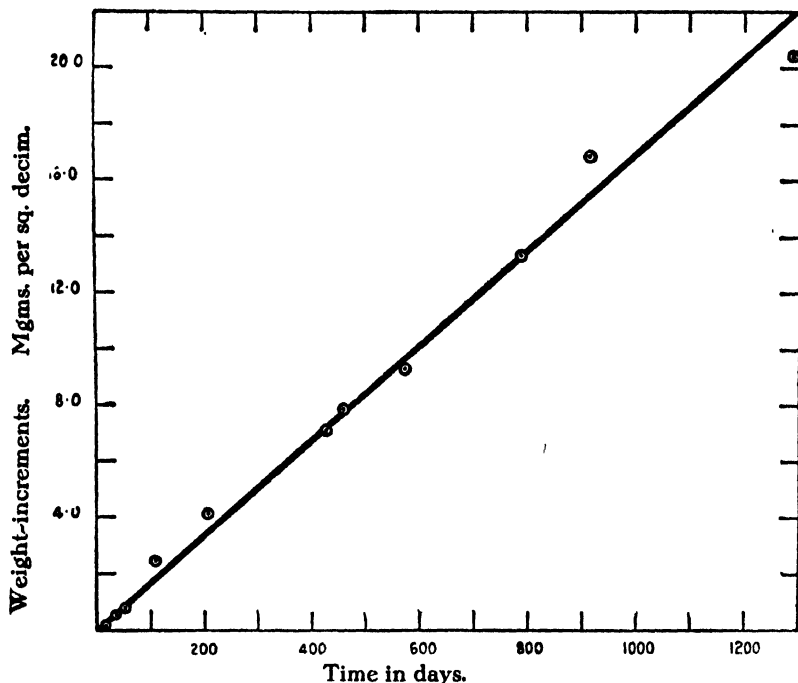


Fig. 10.—Oxidation of zinc at the ordinary temperature. Relation between weight-increment and time. "Long Period."

effect upon the surrosion of zinc. Thus, the reason for the continuity of the curve is radically different from that which obtains in the case of copper.

### (3) Note upon Effect of Surface Condition.

In the First Report (*loc. cit.*, Table I, p. 860) it was shown that up to 205 days' exposure the difference in behaviour between zinc specimens with a dull emiered surface and those which had been brightly polished to a "mirror finish," was extremely small. It may now be noted that after an exposure of 1300 days, "dull" and "bright" specimens showed weight-increments of 20.8 and 20.5 mg. per sq. dm. respectively. On the other hand, copper specimens exposed simultaneously gave for "dull" and "bright" surfaces respectively, weight-increments of 5.4 and 4.3 mg. per sq. dm.

#### (4) Note upon Visual Results.

The absence of interference colours from the surface of zinc which is undergoing "surrosion" is clearly in harmony with the linear nature of the weight-increment curve, which indicates a product having a granular or discrete structure as distinct from the continuous envelope which gives rise both to interference colours and to a parabolic weight-increment curve. Nevertheless it will be observed that the possibility of *diffraction colours* is not excluded. It is of interest to note that the only colour effects which have been observed upon zinc, whilst quite inexplicable on the interference view, become completely intelligible when regarded from the point of view of diffraction. In the First Report (*loc. cit.* 857) the development of a "sky-blue" border was noted; specimens exposed more recently have shown a distinct blue tinge over the whole surface. Now in the case of a film which is gradually increasing in thickness and causing interference colours to be produced, light waves will be extinguished in the order of their lengths, the shortest being the first affected; hence emergent light will at first correspond to the colours of the longer waves (yellow, orange and red) and therefore blue will not be expected till this sequence has been passed. But in the case of diffraction, the colour will depend entirely upon the spacing of the granules in the reaction-product and, hence, would be expected to be relatively independent of the period of exposure. There can be little doubt therefore, that the blue colour associated with the surrosion of zinc is a diffraction effect such as would normally be expected from the gravimetric data.

#### (5) Microstructure of Surrosion-Films upon Zinc.

Hitherto the view that the film of reaction-product upon zinc partakes of a "granular" or "cellular" nature, has been inferred from the linear disposition of the weight-increment curve. Direct evidence has now been obtained, however, by microscopical examination of the film. The photomicrograph reproduced in Fig. 11 was obtained from a zinc specimen which had been exposed in the "basement" atmosphere for 18 months. It will be seen that the granular structure is actually quite distinct. In addition it may be noted that there is now a slight indication of the underlying crystal structure, some crystal grains appearing darker than others, suggesting selective rates of attack due to differences in orientation.

It is instructive to compare this photomicrograph with Fig. 22 of the First Report, which shows the appearance of tarnished copper under the microscope. The comparison brings out clearly the fundamentally different nature of the two films, upon which the whole course of the oxidation process in each case depends.

#### B. ATMOSPHERE TYPE 2.—"TANK ROOM."<sup>22</sup>

*Relation between Weight-Increment and Time.*—The results available at the time of the First Report suggested the "possibility" of an acceleration in the rate of attack upon zinc exposed in the "tank room" quite apart from any acceleration due to increasing corrosivity of the atmosphere (First Report, *loc. cit.*, 869). More extended observations, however, have failed to confirm this suggestion. On the contrary the results now plotted in Fig. 13 (representing 1200 days' exposure) and also results yielded by other specimens for similar periods have shown that the straight line relationship

<sup>22</sup> For description, see First Report, *loc. cit.*, p. 853.

has been followed extremely closely, having regard to the relatively severe fluctuations in external conditions.

*Rate of Attack as compared with Rate of Attack in Atmosphere Type 1.*—The linear relationship between weight-increment and time having been shown to apply to exposure in both types of atmosphere, even after comparatively lengthy periods, comparison of the respective rates of attack is obviously facilitated. Typical data are included in Table IV.

TABLE IV.

RATE OF ATTACK UPON ZINC EXPOSED IN "BASEMENT" AND "TANK-ROOM" RESPECTIVELY.

Atmosphere.	Series No.	Period of Exposure. Days.	Mean Total Weight Increment. Mg. per Sq. Dm.	Rate of Attack. Mg. per Sq. Dm. per 1000 Days.
Type 1 "Basement"	4B.	1160	18.7	16.1
	9B.	1300	20.6	15.9
	10B.	830	13.8	16.5
Type 2 "Tankroom"	4T.	1205	9.1	7.5
	10T.	1100	10.6	9.5

It is somewhat surprising that under the relatively dry conditions of the "basement" the rate of attack upon zinc is considerably greater than that which obtains under the relatively humid condition of the "tank-room." The most probable explanation, however, is that the divergence in behaviour is a temperature effect (see First Report, Fig. 1) and that the influence of humidity, within the limits represented by the present conditions, is a neutral one.<sup>23</sup>

### SECTION III.—BRASS.

#### (a) Relation between Weight-Increment and Time.

*Atmosphere Type 1.*<sup>24</sup>—In the First Report (*loc. cit.*, p. 864), the following statement was made. "Results of tests upon 70/30 and 60/40 brass for a period up to 450 days, the first weighing having been conducted 144 days from the start, have given points lying almost exactly upon a parabola." In Fig. 12 are now given the results obtained from these *same specimens* during a period of 1660 days, the squares of weight-increment being plotted separately; the graphs yielded by a single copper specimen exposed simultaneously are also included. The statement quoted above remained true in the case of 70/30 brass for about a further 100 days, after which weight-increments were in excess of those required by the parabola. In the case of the 60/40 brass the defection from the parabola appears already to have commenced when the statement was made. In each case the subsequent course followed was, within experimental error, a straight line. On the other hand, even after this lengthy period of exposure, copper has still adhered closely to the parabola.

<sup>23</sup> Definite results obtained in connection with the rusting of iron (see Section 7) suggest that for each corrosion product there is a *critical atmospheric humidity* above which moisture condenses upon the specimen, and below which variation in the content of water vapour is without appreciable influence.

<sup>24</sup> For description see First Report, *loc. cit.*, 853, present report, p. 117.

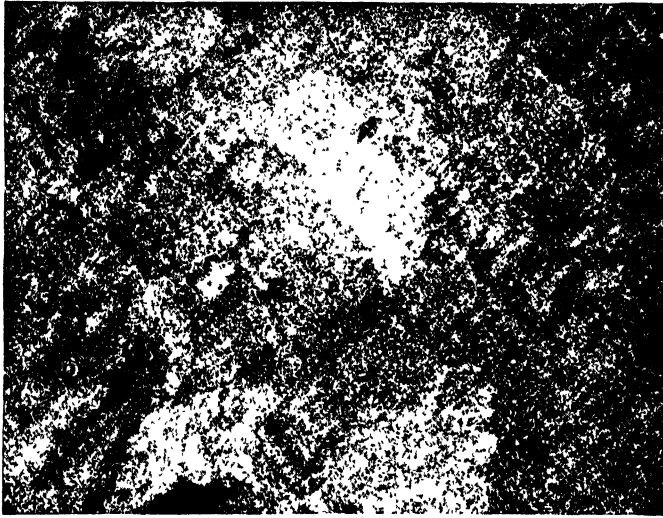


Fig. 11.—Zinc, after exposure to indoor atmosphere as described in text.  
× 150 diams.

*[To face page 140.]*

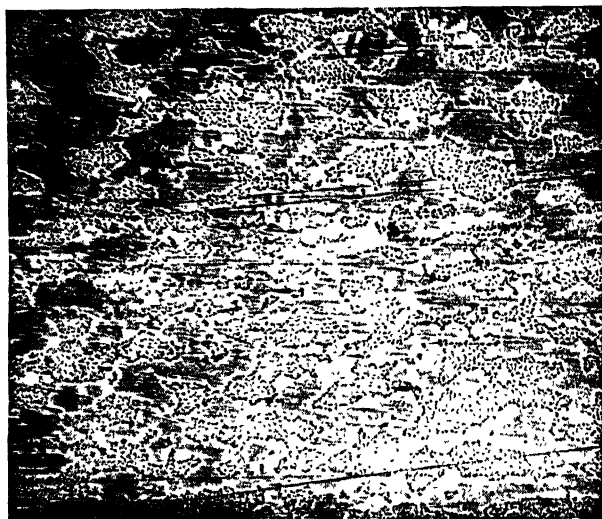


Fig. 14 -60/40 Brass, after exposure to indoor atmosphere as described in text

× 150 diams

[To face page 111.

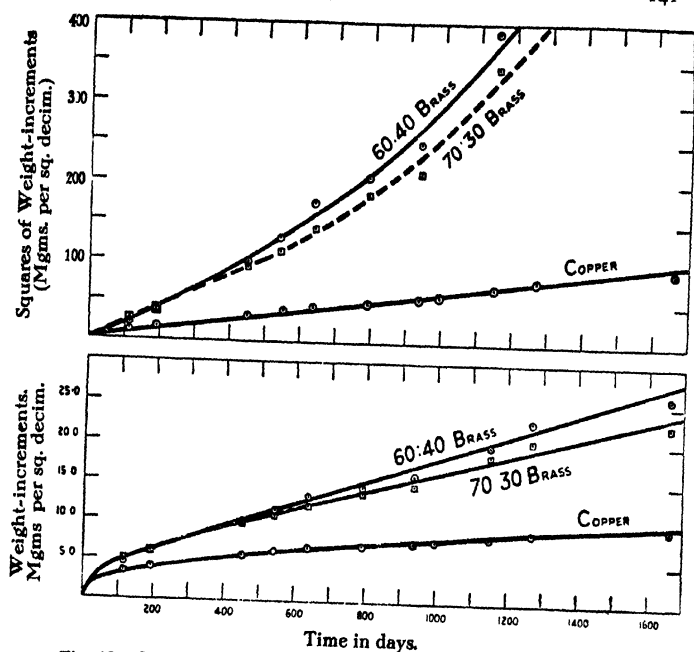


Fig. 12.—Oxidation (tarnishing) of Copper, 70/30 and 60/40 Brass. Atmosphere Type 1. "Long Period." Relation between weight-increment and time.

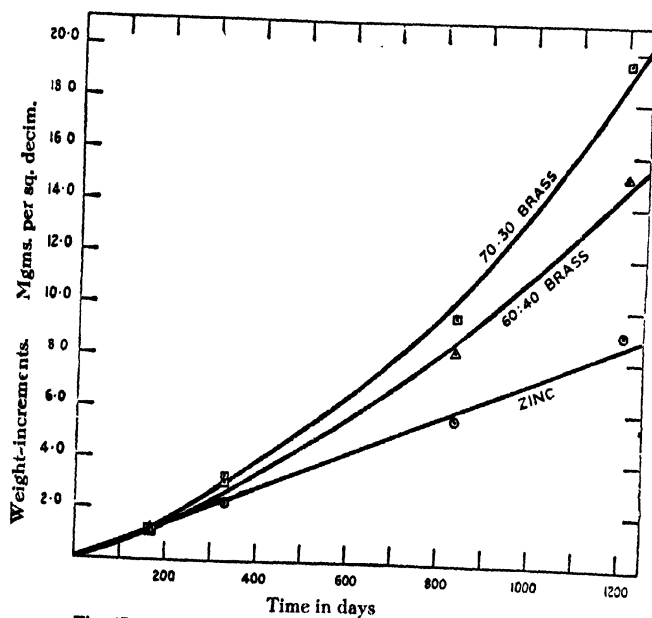


Fig. 13.—Relative behaviour of 70/30 and 60/40 Brass and Zinc in Atmosphere Type 2. ("Tank-room").

The position to date, therefore, is that while in the present type of atmosphere zinc and copper have given no indication whatever of any departure from the straight line and parabola respectively, 70/30 and 60/40 brass behave anomalously. Although for a time they resemble copper and yield a curve which approximates to the parabola, after more extended exposure they revert to the straight line which is characteristic of zinc.

*Atmosphere Type 2.*<sup>24</sup>—Under the more humid conditions of the “tank-room” the tendency referred to above for brass to follow the parabolic behaviour of copper seems entirely to disappear. So far as the observations have gone there is at no stage any indication of a falling off in the rate of attack; on the contrary there appears to be definite evidence of acceleration. This is shown in Fig. 13, where results from specimens of 70/30 and 60/40 brass after 1200 days’ exposure are plotted, together with results from zinc exposed simultaneously. The approximately linear relationship maintained by the zinc suggests that there has been no appreciable increase in the corrosivity of the atmosphere. Possibly the increased rate of attack upon the brasses may be accounted for by the selective deposition of moisture upon the respective corrosion products.

#### **(b) Relation between Weight-Increment (Corrosion) and Composition.**

Atmosphere Type 1.	See Section 4(a), p. 146.
Atmosphere Type 2.	See Section 4(b), p. 146.
Domestic Kitchen.	See Section 4(c), p. 146.

#### **(c) Microstructural Changes on Atmospheric Exposure.**

The microscopical examination of 60/40 brass at various stages of exposure brings out several interesting points. In the early stages of exposure in atmosphere Type 1, the attack is directed almost entirely upon the *alpha* constituent which develops an apparently continuous tarnish film in the same way as copper. During this time, indeed, the alloy behaves in a similar manner to copper and tends to follow a parabolic curve. Later on, however (coinciding approximately with the appearance of the “fogging effect” described in the First Report, *loc. cit.*, p. 856), an attack of quite a different type develops upon the *beta* constituent; the effect is discontinuous over the surface, and gives rise to an apparently duplex structure. This is shown in the photomicrograph reproduced in Fig. 14. There can be little doubt that this phenomenon marks the early stages of the departure from the parabola to the straight line which has been referred to in connection with the gravimetric results (“a” above).

#### **(d) Properties of Oxide Films Developed in Relatively Pure Atmosphere at Ordinary Temperatures.**

In view of the remarkable protective properties of the film developed upon copper during the “summer period,” interest attaches to the behaviour of brass when exposed under similar conditions. It will be recalled that intensive weighings upon copper specimens showed that the parabola of relatively low rate constant obtained during the summer or non-tarnishing period, was entirely undeflected on emerging into the period of relatively high tarnishing capacity. The specimens, from which the results

plotted in Fig. 15 were obtained, including representatives of 70/30 and 60/40 brass and, also, of copper, were first exposed on June 19th, (1923) and hence had the maximum time for the development of any protective film. (In the figure the approximate division between the summer and winter period is indicated by a vertical line.) During the summer period it so happened that the weight-increments yielded by the various specimens were almost identical, a circumstance which lends additional interest to the remaining portion of the diagram. It will be seen that although agreeing so closely in weight the respective films differ considerably in properties. Only in the case of copper does the parabola continue undeflected through the period representing the more drastic conditions of

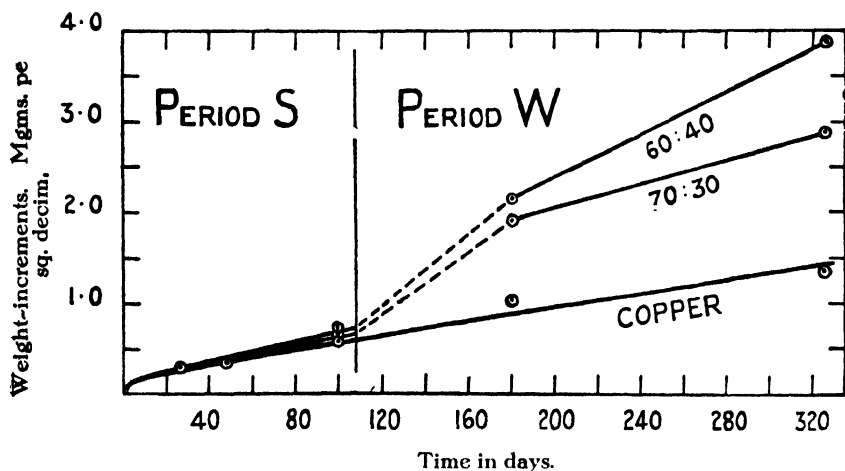


Fig. 15.—Copper, 70/30 brass, 60/40 brass Atmosphere Type 1. Relative protection afforded during Period W by thin films of oxide developed during Period S. (Compare Fig. 1)

exposure, a result which confirms those previously recorded as to the imperviousness of the film. In the case of each of the brasses there is a very considerable increase in the rate of attack, showing that the earlier film is not proof against the altered atmospheric conditions, *i.e.* the efficiency of any protective effect must be extremely small.

#### (e) Properties of Oxide Films Developed at Temperatures Above Normal.

Experiments have been conducted to determine whether by exposure to air at temperatures above normal an oxide film could be developed upon brass sufficiently impervious to afford protection against tarnishing on subsequent exposure. A preliminary set of heat-treatment experiments upon 70/30 and 60/40 brass showed that very similar visible effects were produced on each alloy for the same temperature of heating; in order to try out the more extreme case first the experiments were continued upon 60/40 brass only. These experiments were projected upon exactly the same lines as those described for copper and the results to date were included in the communication previously referred to (*loc. cit.*).

*Immediate Effects of Heat-Treatment.*—A uniform time of heating of one

hour was employed throughout. For equivalent thickness of film, considerably higher temperatures were required than was the case with copper; *e.g.* to produce a darkening of the metal approximately equivalent to that obtained by heating copper at 100°, brass specimens required to be heated at 200°, after which treatment, although slightly darkened, they were still pale yellow in colour. Increasing the temperature of heat-treatment progressively to 350° merely increased the depth of yellow, but between this temperature and 400° a neutral or steely tint was obtained. At 425° a second-order yellow appeared, accompanied, however, by specks of zinc oxide, indicating the end of the interference colour range.<sup>25</sup>

*Subsequent Effects of Heat-Treatment.*—Available evidence as to the protective effect of oxidation is not so conclusive as that which has been recorded for copper. This is particularly true of the gravimetric results, as will be seen by reference to Fig. 7, where subsequent weight-increments of brass specimens after 100 days' exposure are plotted against the temperature of heat-treatment; corresponding data for copper are included on the same diagram. Although the first heat-treated member of the series (200°) has suffered definitely less attack than the unheated "blank," the reduction is considerably less than that which obtained for copper heated at 75°. Moreover, the weight-increment progressively increases as the temperature of heat-treatment rises (in contradistinction to the behaviour of copper) until, with the specimen heated at 250° the increase is very little less than that suffered by the unprotected "blank." Nevertheless, the visible results were much more satisfactory than these figures would suggest. Thus, after 28 days' exposure untreated specimens had darkened considerably, with development of light-brown patches, whilst the specimen heated at 200° had apparently undergone no change. As a result, the treated specimen appeared much lighter than the untreated blank, although when first exposed it was a shade darker owing to the effects of the heat-treatment; the remainder of the specimens appeared to have undergone no further change. After 100 days, untreated specimens had become yellowish-brown generally; there was marked contrast between these and the specimen heated at 200° which was still pale yellow, whilst the remaining specimens had altered but very little in appearance since the first exposure.

It will be seen, therefore, that although oxide films upon brass are not so efficacious as those upon copper, there is definite evidence that the protection extends to brass, the effects being confined mainly to the suppression of further colour changes.<sup>26</sup>

#### (f) Use of Lanoline for Protecting Brass Exposed to "Dew-Point" Conditions.

The tests to be described were started as far back as November, 1922, since when the specimens have been exposed to the atmosphere of the "tank-room." The results are of interest in view of the conclusions already discussed as to the susceptibility of brass to attack by this type of atmosphere (see p. 142). In the present instance, however, the material employed

<sup>25</sup> For weight-increments and other details, the original paper may be referred to.

<sup>26</sup> The experiments described in the text were suggested by the results which had already emerged from the systematic work upon copper. The earlier work of Bengough and Hudson (English Patent, 1917, *J. Soc. Chem. Ind.*, 1919, 640 A.) may be recalled, however, in which protection against attack by sea-water was obtained by a preliminary oxidation of the brass in air, at a temperature not exceeding 450° C. Alternatively, immersion in a solution of permanganate, or an aerated solution of carbonate, was recommended.

contained only 10 per cent. zinc.<sup>27</sup> Direct results upon 70/30 or 60/40 brass would no doubt have been advantageous. Actually, however, the results yielded by the (unprotected) 90/10 brass were similar in type to those obtained from the standard brasses under similar conditions; there can be little doubt that the treatment would be equally effective if applied to these materials.

*Method of Treatment and Initial Effects of Lanoline.*—Two specimens (each “dull-polished” and in the hard and annealed condition respectively) were immersed in a bath of molten lanoline at 100° C. They were allowed to drain in a steam-oven for some hours<sup>28</sup> and finally as much as possible of the lanoline removed by wiping with cotton-wool. The weight of the lanoline remaining was 4.7 and 5.0 mg. on the hard and annealed specimens respectively. This treatment had the effect of darkening the plates rather considerably as will be seen from the following reflectivity values:—

TABLE V.

EFFECT OF TREATMENT WITH LANOLINE AT 100° C. UPON REFLECTIVITY OF BRASS SPECIMENS.

		Reflectivity Per Cent.		Loss Per Cent.
		Before Treatment.	After Treatment.	
Hard specimens	Front	44.8	24.3	46.0
	Back	63.0	36.7	42.0
Annealed specimens	Front	68.0	42.8	37.0
	Back	73.0	47.8	34.5

*Subsequent Protective Effects.* (a) *Visual and Optical.*—Although when first exposed the “lanolined” specimens were much darker than the rest, on subsequent exposure they appeared to undergo no further change and at the end of six weeks they appeared far more like the original brass than any of the other specimens. The protection afforded by the lanoline is also shown by the following reflectivity figures:—

*Mean loss of Reflectivity during 6 weeks' exposure.*

Untreated specimens . . . 47.2 per cent.

Treated specimens . . . 17.8 „ „

(b) *Gravimetric.*—At the end of the 1400 days the weight-increment of untreated specimens showed little variation and gave the mean value of 15.0 mg. per sq. dm. On the other hand the weight-increment of the (hard and annealed) lanolined specimens were 6.8 and 7.9 mg. per sq. dm. respectively. The conclusions reached in the early stages as to the protective value of the treatment with lanoline thus receives adequate confirmation.

<sup>27</sup> At the time the experiments were started this was the only alloy available in sufficient quantity to satisfy the complete objects of the tests, which included, not only the effect of lanoline treatment, but also the effect of various methods of preparing the original surface. In the latter respect the results showed remarkable uniformity, as will be seen by reference to Appendix B of the First Report (*loc. cit.*, p. 893), where the optical results at 14 days are given in full for the whole series—excluding those which had been treated with lanoline.

<sup>28</sup> Actually in the attempt to drain off the whole of the lanoline; this, however, was found to be impracticable.

## SECTION IV.

*THE RELATIVE BEHAVIOUR OF COPPER, ZINC, AND BRASS, EXPOSED TO SEVERAL TYPES OF INDOOR ATMOSPHERES.***(a) Exposure in Atmosphere Type 1 ("Basement").**

In the First Report (*loc. cit.*, Fig. 7), the weight-increments yielded by representatives of the zinc-copper series at 15, 36 and 205 days' exposure were plotted against zinc content. Results up to 916 days are now plotted in Fig. 16, but for the sake of simplicity only one set of curves (those which refer to emiered specimens), is included. The diagram brings out clearly the increasing disparity in the surrosion of copper and zinc respectively.<sup>29</sup> The explanation lies of course in the fact that during the whole time copper has followed the parabola, whilst zinc has followed the straight line. That the high-zinc brasses have approached relatively nearer to the zinc in respect to their position on the diagram is also accounted for by the fact that after prolonged exposure these alloys leave the parabola upon which they started in the early stages and follow the straight line as for zinc.

**(b) Exposure in Atmosphere Type 2 ("Tank-room").**

It will be recalled that the chief feature of the atmosphere of the "tank-room," as distinguished from that of the "basement," is its relatively high, and fluctuating, humidity. In addition, however, for the greater part of the year the mean temperature is appreciably lower than that which obtains for the "basement" (see First Report, Fig. 1). Increasing humidity naturally favours condensation of moisture, but it should be remembered that whether moisture is actually precipitated, or not, will also depend upon specific properties of the corrosion product. Results obtained from copper, zinc, and the two standard brasses after an exposure of 1200 days in the "tank-room," are plotted in Fig. 17. It will be seen that the difference in behaviour between copper and zinc is less marked than was the case in the "basement." Moreover, the intrinsic attack is considerably less, an effect presumably attributable to the reduced temperature; clearly, however, any effect due to increased humidity must have been extremely small. On the other hand, the attack upon the brasses is now greatly in excess of that upon either copper or zinc, and also (in spite of the lower temperature), in excess of that undergone by the same materials exposed to the "basement" atmosphere for a similar period. In this case, therefore, it is highly probable that the increased attack has been brought about by a selective precipitation of moisture.

**(c) Exposure in Domestic Kitchen.<sup>30</sup>**

It is evident that under the conditions of a domestic kitchen relative humidity will be subject to considerably wider fluctuations than is the case with either of the atmospheres previously considered; precipitation of moisture upon the specimens will inevitably take place at more or less frequent intervals. The position is rendered still more complex by the products

<sup>29</sup> It is instructive to compare this diagram with the earlier one, bearing in mind the great difference in the vertical scales.

<sup>30</sup> See First Report, *loc. cit.*, p. 855.

of combustion (in this case principally those of coal-gas), which are emitted directly into the room.

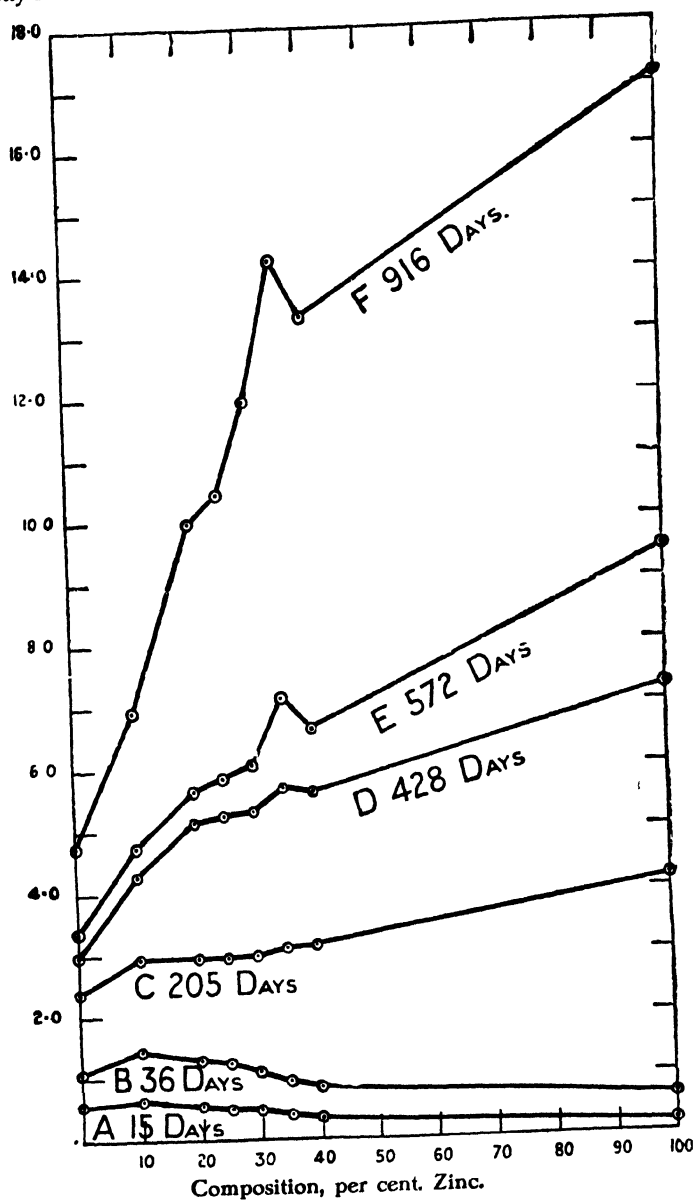


Fig. 16.—Zinc-copper Series. Weight-increments at various periods. Atmosphere Type 1.

N.B.—Curves A, B and C were plotted (on a more open vertical scale) in Fig. 7 of the First Report.

Under such conditions specimens of copper, 70/30 and 60/40 brass and zinc, have been exposed for a period of 1230 days. Each material

was represented by two specimens, in the emiered and brightly-polished condition respectively, their dimensions being the same as in (a) and (b) above, *i.e.*  $10.0 \times 10.0$  cm.

For the purpose of comparison a similar pair of iron plates (ordinary ingot iron)<sup>31</sup> was included, but for a rather shorter period (1150 days). No corrosion product was observed to leave any of the non-ferrous specimens, but for the greater part of the time there was a steady fall of rust from the iron.

When dismantled, the copper and zinc specimens showed little if any sign of moisture, but the brasses, more particularly 70/30, were distinctly moist, owing no doubt to the hygroscopic nature of the corrosion-products. Each specimen was then carefully scraped with a blunt tool, for the purpose

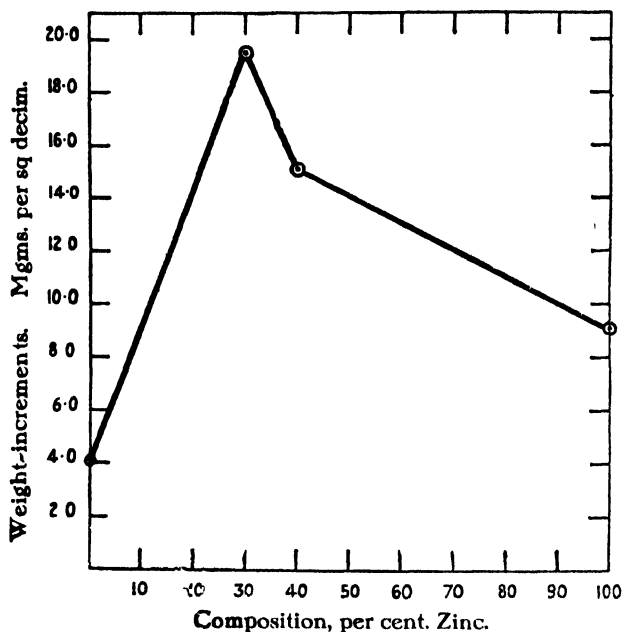


Fig. 17.—Relative corrosion (weight-increments) of copper, 70/30 brass, 60/40 brass, and zinc, after 1200 days exposure in "tank-room."

of removing the corrosion-product as completely as possible, at the same time avoiding undue interference with the underlying metal. The products so removed were carefully collected and subjected to analysis (see results below); the specimens were finally desiccated and weighed. Losses of weight (mg. per sq. dm.) were as follows:—

Copper	Bright	6.0	7.2	Zinc	Bright	30.8	27.8
"	Dull	8.4			"	Dull	24.8
Brass 70/30	Bright	177.8	164.2	Iron	Bright	739.2	682.9
"	Dull	150.6			"	Dull	626.6
60/40	Bright	37.4	33.5				
"	Dull	29.7					

The mean losses (non-ferrous materials), are plotted in Fig. 18, which should be compared with Figs. 16 and 17, bearing in mind that ordinates

<sup>31</sup> See p. 165.

represent *loss of weight* in Fig. 18, and the usual increase in weight in the other cases; the very great numerical difference in the vertical scales should also be noted. As would be expected, there is a broad general resemblance to the "tank-room" curve, 70/30 occupying the "peak" in each case. The attack upon the 70/30 brass, however, is now excessively greater than that upon any of the other materials, an effect which, presumably, may be attributed to the incidence of products of combustion.<sup>32</sup>

*Analysis of Corrosion Products.*—The complete analyses are set out in Table VI. The "dezincification" of the brasses is shown by the preponderance of zinc in the products and is excessive in the case of 60/40 brass. The high content of sulphate, more particularly in the products from copper and 70/30 brass, will be noted. An interesting feature is the

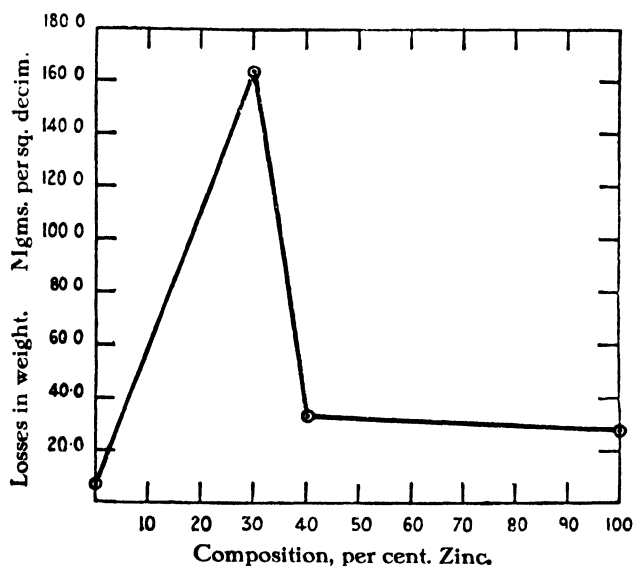


Fig. 18.—Relative corrosion (losses in weight) of copper, 70/30 brass, 60/40 brass, and zinc, after 1200 days exposure in domestic kitchen.

appearance of *combined organic acid radicles*. They were determined by extraction of the fatty acid with ether, after hydrolysis with hydrochloric acid. (Only in the case of 60/40 brass was any free fatty matter present, as shown by treatment with ether before hydrolysis.) The further interesting result may be noted that the proportion of combined organic radicles increases with the zinc content, suggesting that they are present in combination with zinc. A rough determination of the mean molecular weight of the associated fatty acids gave a value of 134, a relatively low value, indicating a correspondingly high vapour pressure, as would of course be expected.

<sup>32</sup> In interpreting Fig. 18, the dezincification of the brasses (see analyses of corrosion products) should be borne in mind. As will be discussed more fully in Part II., this represents a definite amount of corrosion which is not included in the figure for loss in weight; hence the actual attack upon the brasses no doubt exceeds that upon copper or zinc to a greater extent than is shown by Fig. 18. Moreover, in view of the excessive dezincification of 60/40 brass, the curve in Fig. 18 probably exaggerates the disparity in the actual corrosion of 70/30 and 60/40 brass respectively.

TABLE VI.

COPPER, ZINC, 70/30 AND 60/40 BRASS. ANALYSIS OF CORROSION PRODUCTS AFTER 176 WEEKS' EXPOSURE IN A DOMESTIC KITCHEN.

A. Moisture driven off at 100° C. Matter insoluble in acids. Percentage values.

	Copper.	70/30 Brass.	60/40 Brass.	Zinc.
H <sub>2</sub> O . . . . .	14.5	16.1	15.7	13.4
Insoluble matter . . . .	1.5	1.0	1.5	2.4

B. Metallic and non-metallic radicles in product after drying. Percentage values, excluding insoluble matter.

Cu . . . . .	25.5	23.6	3.4	—
Zn . . . . .	—	24.6	39.7	41.2
[SO <sub>4</sub> ] . . . . .	29.2	30.2	16.1	15.2
[S] . . . . .	0.3	0.42	2.4	0.66
[CO <sub>2</sub> ] . . . . .	4.9	2.3	7.4	5.1
Combined fatty acid radicles . . . . .	Not estimated } Probably nil }	1.9	3.9	6.4
Free fatty matter . . . . .		nil.	1.6	nil.
[OH] and combined H <sub>2</sub> O } (By difference)	40.1	17.0	25.5	31.4

## SECTION V. ALUMINIUM.

### (a) Introduction.

The primary object in undertaking these experiments was to determine the precise form of weight-increment curve yielded by aluminium on oxidation at the ordinary temperatures, so that the information might be collated with that already obtained for other metals. Possible difficulties, not met with hitherto, were anticipated at the outset. Thus, it is generally believed that a freshly-cleaned surface of aluminium becomes rapidly covered with a film of oxide which tends to retard further oxidation. In the main, however, the evidence is of an indirect character and, so far as the author is aware, there has been no previous attempt to trace the formation of the film at ordinary temperatures by direct weighing.<sup>33</sup>

### (b) Experimental.

*Atmosphere.*—The tests to be described were conducted entirely in Atmosphere Type 1. (see p. 117).

*Specimens.*—For the bulk of the experiments high-grade metal containing 99.6 per cent. aluminium was employed.<sup>34</sup> Tests have also been conducted upon aluminium of exceptional purity, prepared by the Hoopes electrolytic refining process.<sup>35</sup> Specimens having the uniform dimensions of 10.0 × 10.0 cm. have been used throughout. The preparation of the surface occasioned some preliminary investigation, since the treatment with

<sup>33</sup> The high temperature oxidation of aluminium has been investigated by Pilling and Bedworth (*J. Inst. Metals*, 1923, 29, 573), who found that at 600° C. the oxide film increased in thickness during sixty to eighty hours, after which no further appreciable weight-increment occurred even after prolonged heating. Assuming a normal density, the thickness of the film was then approximately 0.00002 cm.

<sup>34</sup> Kindly supplied by the British Aluminium Company.

<sup>35</sup> See J. E. Edwards (*Trans. Amer. Electrochem. Soc.*, 1925, 47), where the typical figure of 99.98 per cent. aluminium is given.

fine emery paper which had served so well for copper was found to be quite unsuitable; particles of emery embedded themselves in the surface and could not be removed by ordinary methods. The treatment decided upon really consisted of "dry scratch-brushing." Using a steel wire brush it was found that any pre-existing scale could be thoroughly and rapidly removed and quite a fine "silky" surface imparted to the metal. Immediately following the final treatment with the wire-brush the specimen was brushed quickly with a flat camel-hair brush to remove particles of abraded metal and then transferred as expeditiously as possible to a desiccator, which was at once evacuated. In addition to the vacuum (oil) pump, connection was also made to a nitrogen cylinder, and by alternately filling with nitrogen and evacuating several times, finishing with a vacuum (approx. 1 mm.) the removal of all air from the desiccator was ensured. Each experiment was performed in duplicate, but usually a separate desiccator was used for each specimen. The desiccators were left overnight at the side of the balance.

*Weighing.*—The Conrady system of weighing was employed as in the copper experiments (see p. 118). On account, however, of the very appreciable "buoyancy effect" introduced by the difference in density between the specimens and the brass weights, the effect of fluctuations of barometric pressure and also of temperature had now to be taken into consideration and an appropriate correction was applied to each weighing.<sup>36</sup> In order to illustrate the data involved a portion of a table of results is reproduced in Table VII.

TABLE VII.

ALUMINIUM, GRAVIMETRIC RESULTS CORRESPONDING TO PORTION OF FIG. 19.  
EXAMPLE OF EXPERIMENTAL DATA.

Date.	Mark. <sup>37</sup>	Period of Exposure.	Apparent Weight. Grams.	Thermom. Reading. °C.	Barom. Reading. mm.	Correc-tion. <sup>38</sup> mg.	Corrected Weight. Grams.	Weight-Increment mg. (actual) = mg. per 2 sq. dm.
Nov. 17	Al/H <sub>4</sub>	(5 gm. added) <sup>39</sup>	50.30547	20.0	771.6	2.59	50.30806	—
"	Al/S <sub>4</sub>	(6 gm. " ) <sup>39</sup>	50.83124	20.8	771.3	2.55	50.83379	—
"	AM/H <sub>2</sub>	(6 gm. " ) <sup>39</sup>	50.429375	20.5	771.6	2.56	50.431935	—
"	AM/A <sub>2</sub>	(6 gm. " ) <sup>39</sup>	50.96211	20.7	771.4	2.55	50.96466	—
"	Al/H <sub>4</sub>	8 hours	50.30563	20.3	772.3	2.58	50.30821	0.15 } .18
"	Al/S <sub>4</sub>	"	50.831405	20.2	772.5	2.59	50.833995	0.205 } .18
"	AM/H <sub>2</sub>	"	50.429465	20.3	772.5	2.585	50.43205	0.115 } .13
"	AM/A <sub>2</sub>	"	50.96221	20.2	772.5	2.59	50.96480	0.14 } .13
Nov. 18	Al/H <sub>4</sub>	1 day	50.305695	20.2	773.9	2.615	50.30831	0.25 } .245
"	Al/S <sub>4</sub>	"	50.83144	20.8	773.6	2.59	50.83403	0.24 } .245
"	AM/H <sub>2</sub>	"	50.42952	20.5	773.9	2.60	50.43212	0.185 } .19
"	AM/A <sub>2</sub>	"	50.96226	20.6	773.8	2.60	50.96486	0.20 } .19

<sup>36</sup> The importance of this procedure will be appreciated when it is stated that it was by no means unusual for the apparent weight of the specimen after exposure (even for as long as ten days) to be less than the apparent initial weight.

<sup>37</sup> Al/H<sub>4</sub> = Specimen containing 99.61 per cent. Al (see p. 150). Hard-rolled.

Al/S<sub>4</sub> = " annealed.

AM/H<sub>2</sub> = Specimen containing 99.98 per cent. Al (see p. 150). Hard-rolled.

Al/S<sub>4</sub> = " annealed.

<sup>38</sup> The correction as used is short of the correction necessary to bring to the *true weight in a vacuum* by 12.0 mg. throughout.

<sup>39</sup> These weights were added to the specimen side of the balance for the purpose of maintaining a constant load throughout.

## (c) Relation between Weight-Increment and Time.

"Short-period" Tests.—From the results plotted in Fig. 19 up to 27 days' exposure, it will be seen that an entirely new type of weight-increment curve is now represented; whilst at the start there is a resemblance to the parabola, this quickly disappears in a "flattening" of the curve towards the horizontal axis.<sup>40</sup> A consideration of the squares of the weight-increments leads indeed to the conclusion that at no time does the curve actually conform to the parabola, *i.e.* the process depends upon an essentially different mechanism from that which has obtained in any of the cases previously considered.

The elucidation of this mechanism, however, presents greater difficulty than heretofore. It is probably not merely a coincidence that the present curve is similar in type to that obtained by various workers in connection

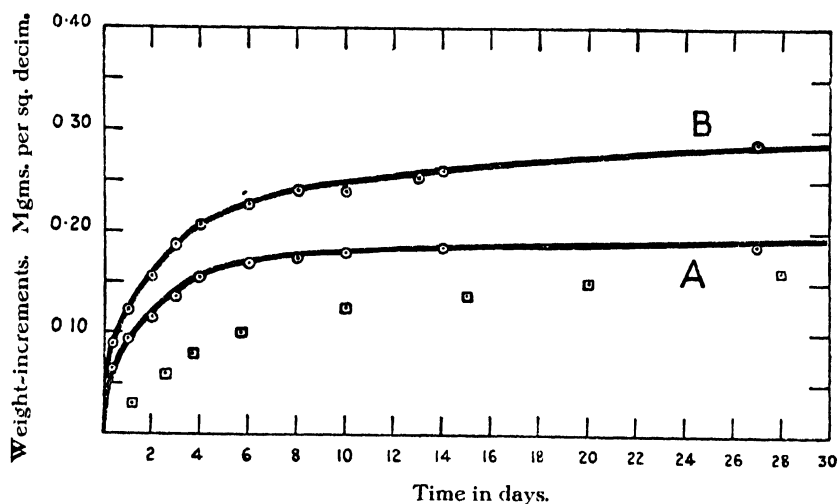


Fig. 19.—Oxidation of aluminium at the ordinary temperature. Relation between weight-increment and time in the very early stages.

A—AM/H<sub>2</sub> and AM/A<sub>2</sub> (see Table 4).

B—Al/H<sub>4</sub> and Al/S<sub>4</sub> ( „ „ ).

[□] = Squares of weight-increments ( $\times 2.0$ ), values taken from Curve B.

with *velocity of adsorption*—*e.g.* of gases and vapours upon charcoal,<sup>41</sup> celluloid,<sup>42</sup> glass,<sup>43</sup> and (perhaps most significant) upon alumina.<sup>44</sup> Various equations have been proposed, increasing in complexity the more nearly they agree with the experimental curve.<sup>45</sup> In discussing the complexity of the factors involved, Freundlich<sup>45</sup> points out that the curve of adsorption velocity cannot be represented by a simply mathematical function and,

<sup>40</sup> If the total weight-increment at ten days' exposure be considered, it is of interest to note that almost exactly half of this took place during the first day, and rather more than one-third during the first eight hours.

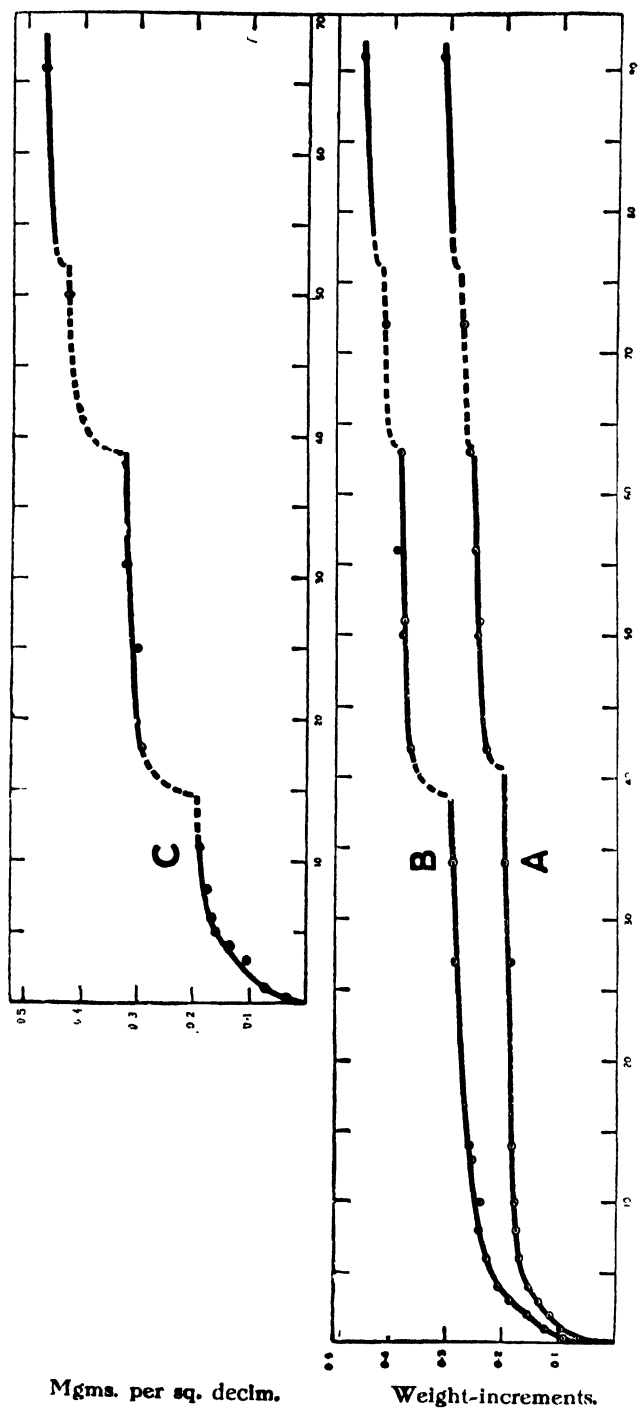
<sup>41</sup> Giesen, *Ann. Physik.*, 1903, 10, 838; Bergter, *ibid.*, 1912, 37, 472; Harned, *J. Amer. Chem. Soc.*, 1920, 42, 920.

<sup>42</sup> Lefebure, *J. Chem. Soc.*, 1914, 105, 328.

<sup>43</sup> Bangham and Burt, *Proc. Roy. Soc.*, 1924, 105A, 481; *J. Physical Chem.*, 1925, 29, 113.

<sup>44</sup> Munro and Johnson, *J. Physical Chem.*, 1926, 30, 172.

<sup>45</sup> *Kapillarchemie*, 1923, 148.



Time in days.

Fig. 20.—Oxidation of aluminium at ordinary temperature. Weight-increment curves ("Long Period"). Partly hypothetical A and B.—Continuation of curves A and B of Fig. 19.  
C.—Mean weight-increments from similar specimens started at a later date. (The curves are in comparable chronological positions).

clearly, the same remark may be extended to the curve now under discussion. The similarity in the curves, whilst strongly suggesting that adsorption is common to the two processes, does not of course permit of a really definite conclusion in regard to the oxidation of aluminium. Possibly the mechanism consists in the formation of an initial film of alumina, with concomitant adsorption of water vapour.<sup>46</sup> In this case the final product would be expected to consist of the hydrated oxide, but experimental verification is difficult on account of the thinness of the film. In one respect at least the disposition of the curve leads to a perfectly definite interpretation, *i.e.* the rapid flattening towards the time axis leaves no room for doubt that the resulting film is extremely impervious in character.

The position may be summed up as follows. The *straight line*: film formation is regulated by gaseous diffusion only, *i.e.* of the atmosphere through the interstices of the granular film. The *parabola*: film formation is regulated by diffusion through a solid envelope. The *present curve*: film formation probably does not depend upon diffusion at all, but upon adsorption. The resulting film is characterised by limited thickness and extreme imperviousness.

*Long-period Tests.*—In the course of the experiments upon aluminium, a somewhat puzzling feature was encountered. Thus, a series of determinations would be carried out, the “flattening” of the curve would be observed and, thenceforward, weighings would be conducted at less frequent intervals. The apparent constancy of the curve would then encourage leaving the specimens for a still longer interval, but on returning a weight-increment would be obtained appreciably in excess of that required by extrapolation of the curve.

The curves reproduced in Fig. 20, representing exposure up to 91 days, illustrate this difficulty, but at the same time they include sufficient determined values to supply a probable explanation. It will be observed that whenever an increase in the weight-increment is obtained in excess of that expected, the curve continues for a time without suffering further alteration—*i.e.* the “flatness” of the curve is retained—until another increase takes place, when again there is a further period without change. It is noteworthy that the “subsidiary increases” are of the same type as the primary increase, *i.e.* the attack takes place very rapidly, but equally rapidly slows down. Finally the conclusion is reached that when the primary film has practically ceased to thicken (after about two weeks under the conditions of the experiments) any further appreciable change takes place through the occurrence of cracks or fissures in the primary film. This explanation would satisfactorily account for the sudden breaks in the weight-increment curve; it would be expected, moreover, that any exposure of the underlying metal would result in the formation of new film, to a smaller extent, but by a similar process to that which was formed originally.

#### (d) Thickness of Surrosion Film—Influence of Purity of Atmosphere and of Purity and Physical Conditions of Metal.

*Influence of Purity of Atmosphere.—Thickness of Surrosion Film.*—For the purpose of computing the relative intensity of attack, it is useful to take the value of the weight-increment when the curve has reached the “nearly flat” stage, some 10 or 14 days after the first exposure. The following

<sup>46</sup> Munro and Johnson, (*Ind. Eng. Chem.*, 1925, 29, 256) found that alumina adsorbed water more readily than any other vapour.

values were obtained at various times of the year, the date of the first exposure being given in each case:—

March	5th	0·17	mg. per sq. dm.
April	24th	0·17	„ „
Aug.	14th	0·14	„ „
„	26th	0·18	„ „
Nov.	2nd	0·15	„ „
„	17th	0·18, 0·24	„ „
Dec.	11th	0·15, 0·22	„ „

The extremely small limits within which the attack on the metal varies, renders it difficult to attach any significance to the differences observed. It is true that the highest values were obtained at a period of minimum atmospheric purity (Nov. 17th and Dec. 11th), but in each case specimens exposed at the same time gave average values. It is probable indeed that the differences observed are really due to differences in the relative freedom from oxide at the time of the initial weighings (since clearly the metal will never be absolutely free from oxide in spite of precautions). On the whole the constancy of the values observed is somewhat surprising.

Including the abnormally high value of 0·24 for Nov. 17th (curve B in Fig. 19), the values range from 0·14 to 0·24 mg. per sq. dm. Accepting a mean value of 0·19, an estimate of the thickness of the corresponding film may be attempted; the result will, of course, depend upon the composition (and density) which the film is assumed to have, but the probable alternatives cannot appreciably affect the order of the value obtained. Thus, taking the alternatives to be anhydrous or hydrated  $\text{Al}_2\text{O}_3$  respectively, on the one hand the density of the crystalline oxide is 3·9; on the other hand the commonest form of the hydrated oxide (*i.e.* the mineral bauxite—probably a mixture of colloidal hydroxides) is usually assumed to have a formula of  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , and a density of 2·55. Introducing these values, the following relationships obtain:—

	$\text{Al}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ .
Increase in weight, mg. per sq. dm.	= 0·19	0·19
Weight of film, mg. per sq. dm.	= 0·404	0·313
Volume of film, c.c. per sq. dm.	= $1·04 \times 10^{-4}$	$1·35 \times 10^{-4}$
Hence, thickness of film, cm.	= $1·04 \times 10^{-6}$	$1·35 \times 10^{-6}$

Thus, in either case the thickness of the film is of the order of a millionth of a centimetre. The meaning to be attached to this value is that it represents the thickness of the “primary film,” *i.e.* before any “subsidiary increases” have taken place.

*Influence of Purity and Physical Condition of Metal.*—As in the case of relative purity of the atmosphere, it is only a negative result which has to be recorded. Experiments conducted with the greatest care employing the two materials described on p. 150 and starting on November 17th (see above, also Fig. 19) showed that the less pure material gave the higher weight-increment. In experiments conducted with equally great care a little later, however (Dec. 11th; above), the position was reversed, the highly pure aluminium then showing the greater increment. Similarly with physical condition; sometimes the hard and sometimes the annealed specimen has appeared to have suffered the greater change, and no definite conclusion can be drawn. As before the differences actually observed may be due to differences in the initial stage of oxidation.

## SECTION VI.—LEAD.

The object of these tests was precisely the same as that stated for aluminium, *i.e.* the determination of the form of the weight-increment curve, concerning which there appeared to be no available information.

## (a) Experimental.

The experiments were conducted in the same atmosphere, and precisely the same methods were followed as for aluminium. The specimens were taken from a sample of exceedingly pure sheet lead.<sup>47</sup> Their dimensions were uniformly 10.0 × 10.0 cm. in area, and their thickness, in most of the tests, approximately 1 mm., giving a weight of just over 200 grams. For the preparation of the specimens, abrasion with emery was clearly even more out of the question than was the case with aluminium, but fortunately the treatment with the wire-brush was found to serve the purpose admirably.

In weighing, the buoyancy correction was again necessary. Weighings were conducted at similar frequent intervals as for aluminium, *i.e.*, from the first 8 hours onwards. Tables of results were identical in form to those for aluminium (see Table VII.), and an example is therefore not reproduced.

## (b) Relation between Weight-Increment and Time.

*Short-Period Tests.*—The curve plotted in Fig. 21, representing the means of closely-agreeing values from duplicate specimens up to 25

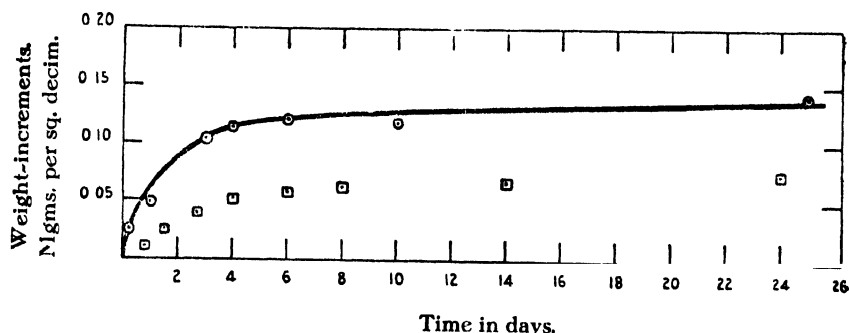


Fig. 21.—Oxidation of lead at the ordinary temperature. Relation between weight-increment and time in the very early stages.

□ = Squares of weight-increments (values taken from smooth curve) × 4.0.

days' exposure,<sup>48</sup> may be taken as quite typical of the results obtained. The similarity between this curve and the aluminium curve of Fig. 19 will be at once apparent; a comparison of the squares of the weight-increments (plotted on each diagram) confirms that they are really of the same type. Clearly, therefore, the considerations already discussed under aluminium apply with equal effect to lead and, again, suggest that adsorption plays some part in the mechanism of film formation. Similar properties in regard to limited thickness and imperviousness may again be attributed to the film.

<sup>47</sup> Supplied by Messrs. Cookson, Newcastle. Analysis 99.995 per cent. lead.

<sup>48</sup> First exposed on April 10th, 1925.

*Long-Period Tests.*—The determination of the weight-increment over comparatively long periods is attended with greater difficulties than in the case of aluminium, and no really satisfactory curves are available. The same phenomenon of unexpected weight-increments has been observed, however, and it is highly probable that the behaviour of the "primary film" on more prolonged exposure is similar for each metal.

### (c) Comparison of Oxidation Values of Aluminium and Lead.

As in the case of aluminium, the intensity of the attack upon the metal may be conveniently estimated by noting the weight-increment when the nearly flat portion of the curve has been reached, for which a somewhat shorter period—about 7 days—is usually required. The value so obtained is appreciably less than in the case of aluminium, the figures ranging from 0.10 to 0.15 mg. per sq. dm., as compared with 0.14 to 0.24 mg. per sq. dm. for aluminium.

Owing to the difficulty of assigning a probable formula to the resulting oxide, no attempt has been made to estimate the thickness of the film in the case of lead, but it is probably of a similar order of magnitude to that which obtains for aluminium.

### (d) Anomalous Behaviour of Lead in Atmosphere Contaminated with Traces of Vapour from Drying Paint.

To appreciate what follows it should be borne in mind that in none of the tests hitherto described (either on lead or aluminium) has any visible change been observed upon the metal. These tests had been in progress for about 7 months, however, when a somewhat extraordinary phenomenon was observed. Specimens of lead which had been recently cleaned and exposed were found to be undergoing a gross attack, the metal rapidly developing a blue colour,<sup>49</sup> and actually becoming *deep blue* in little more than a week. The cause was quickly traced to painting operations in the same building. Exploratory tests upon small specimens suspended over vessels containing the paint, etc., showed that whereas the paint, in bulk, was without effect, rapid tarnishing was induced by paint which was in the process of drying. These experiments suggest that it is the turpentine content which is ultimately responsible for the effects observed, but no attempt has been made to follow the matter exhaustively.

The phenomenon is entirely peculiar to lead in the freshly-cleaned condition. Thus, none of the other materials (aluminium, copper, zinc, etc.) which were exposed in the same room were in the slightest degree affected, as proved by the intensive weighings then in progress; neither indeed were specimens of lead which had already been exposed for a sufficiently long time (this point is discussed below). On the other hand the magnitude of the attack upon freshly-cleaned lead can be gauged from the fact that in 3 weeks<sup>50</sup> such specimens had increased in weight by 3.5 mg. per sq. dm., in striking contrast with the 0.15 mg. per sq. dm. which characterises the attack upon lead under normal conditions during a similar period and following a similar initial treatment.

<sup>49</sup> Presumably a *diffraction* effect.

<sup>50</sup> The attack then rapidly slowed down on account of the suspension of painting operations, shortly after which the attack upon freshly-cleaned lead ceased altogether.

**(e) Protective Properties of Invisible Oxide Films upon Lead.**

In connection with the tarnishing of lead through the causes described above, considerable interest attaches to the fact that if the previous exposure to the unpolluted atmosphere has been sufficiently prolonged, no visible effect is produced upon the metal. In the absence of the actual specimens the phenomenon is best illustrated by reference to Fig. 22. Here Curve A represents the mean weight-increment of two specimens first exposed on April 1st, 1925. Curve B represents, to the same scale and in its correct chronological position (commencing Aug. 13th) the attack upon specimens during the tarnishing period. The enormously greater rate of oxidation exhibited by Curve B will at once be noted, but the point to which

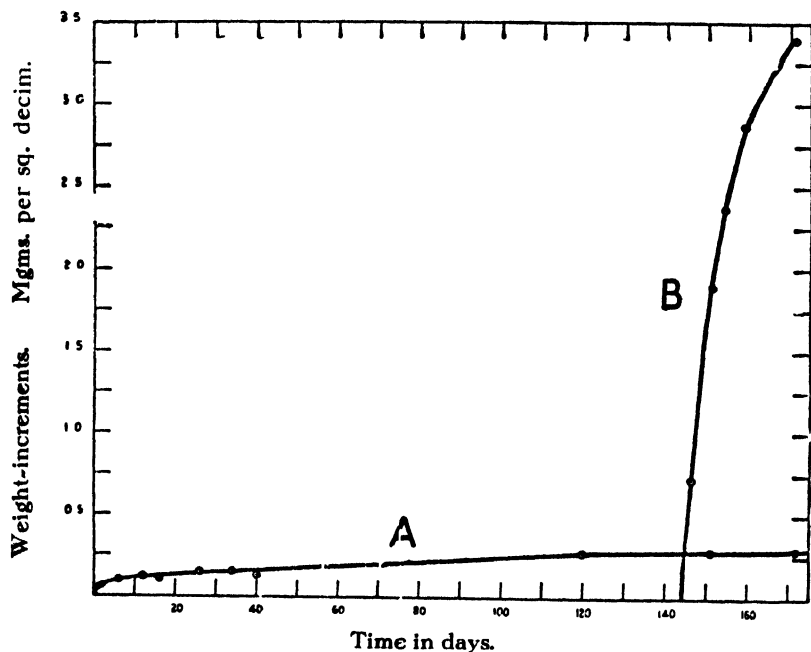


Fig. 22.—Rapid oxidation of lead on exposure to atmosphere containing traces of vapours from drying paint. (Curve B). Immunity of lead which has previously developed a thin film of oxide by exposure to uncontaminated air. (Curve A).

attention is specially drawn is the fact that Curve A, in spite of the smallness of the ordinates, has passed through the tarnishing period without having suffered the slightest deflection. This provides an interesting sequel to the parallel case already discussed for copper (see Fig. 4), and constitutes an even more convincing example of the protection which may be conferred by a thin film of oxide. Once again the condition underlying the production of the non-protective type of film is determined by the incidence of a "foreign constituent" in the atmosphere in excessively small concentration. The nature of this constituent is different in the two cases and the effect is entirely selective upon the metal concerned, but there can be little doubt that the mechanism of the process is essentially the same. The suggestion again arises that the difference between the protective and the non-protective

type of film lies in a relatively small difference in the original lattice. Although no analytical figures are available in the present instance, it is indeed highly probable that the two films, although differing so enormously in physical properties, are really but little different in their chemical composition.\*

### SECTION VII.—IRON.

The tests described in Section 5 of the First Report were started purely for comparative purposes and were admittedly strictly limited. Nevertheless the results appeared to possess sufficient interest to justify some extension of the original experiments.

#### (a) Experimental.

Throughout the recent work specimens measuring 10 cm. × 5 cm. have been employed, *i.e.* half the size of those used originally. They have been prepared by grinding, to remove all traces of pre-existing rust, finishing with the same grade of emery paper (Oakley, O) to ensure uniformity of surface. Particles of emery have been removed by rubbing with pure cotton wool, as described for copper. Finally the specimens have been submitted to an over-night vacuum desiccation and weighed.

Unless otherwise stated the material may be assumed to be the same as that used in the original tests, *i.e.* a commercial ingot iron.<sup>51</sup>

#### (b) Behaviour of Iron in an Indoor Atmosphere of Low Relative Humidity, containing the usual Suspended Solid Particles.—Effect of Filtering the Air, and of Screening the Specimen behind Muslin.

In Fig. 23, Curve B (up to 92 days) represents a typical series of results obtained from the exposure of iron specimens in Atmosphere Type 1, Period W.<sup>52</sup> As already stated<sup>53</sup> the hygrometric conditions were such that the dew-point was exceeded by a wide margin (some 22° F. or 12° C.) during the whole time. The development of rust took place in the characteristic discontinuous manner which was described in the First Report (*loc. cit.*, p. 887, Fig. 22). Subject to the proviso that each speck of rust was surrounded by unaltered iron (evident to visual inspection, especially if aided by a lens), at the end of period W the whole surface was "covered with rust." Considering the relative dryness of the atmosphere, this result, although perfectly typical, appears to be contrary to the prevailing impression that "iron does not rust above the dew-point," an impression which seems to have originated through a too literal application of a principle established<sup>54</sup> under academic conditions for the simple system of air and water-vapour. Clearly, however, ordinary air is a more complex case; in addition to water-vapour and other incidental gaseous impurities it carries suspended *solid* impurities, although normally invisible, in relatively large quantity. Solid particles in the atmosphere are in general hygroscopic through adsorption

<sup>51</sup> The influence of composition (essentially negative under the conditions of the tests) is dealt with later.

<sup>52</sup> The approximate position of the change from "Period W" to "Period S" is indicated on the diagram by a vertical line.

<sup>53</sup> See page 117.

<sup>54</sup> Dunstan, Jowett and Goulding, *J. Chem. Soc.*, 1905, 87, 1548.

of hygroscopic matter<sup>55</sup> and, in the case of town air, many of these are definitely acid through adsorption of acidic matter.<sup>56</sup> It would be expected, therefore, that the deposition of such particles upon a clean iron surface would give rise to corresponding rust centres and, hence, would account for the rusting of the metal above the dew-point.

To test this, two small specimens of iron were polished and placed respectively in glass tubes, one of which was preceded by a filter of pure cotton wool; room air was then drawn through each tube at a similar rate. The experiment was conducted contemporaneously with the exposure of specimens yielding curves as in Fig. 23, and was discontinued after the passage of 100 cubic feet of air (7 days). The specimen over which the filtered air had passed was then still perfectly bright, whilst the other was slightly but definitely rusted—again in the form of isolated “dots” over the surface.<sup>57</sup>

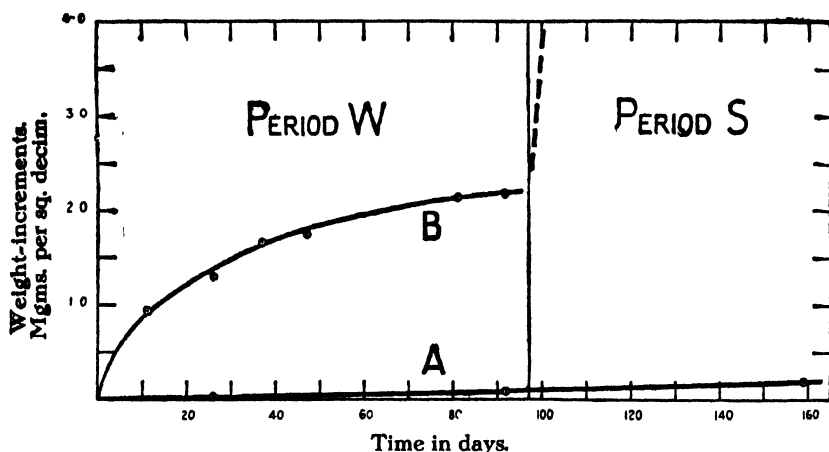


Fig. 23.—Rusting of Iron in indoor unsaturated atmosphere containing the usual suspended solid particles (Curve B). Immunity of iron screened behind muslin (Curve A).

The experiment just described, although conclusive as to the rusting effect of suspended solid matter, clearly suffers from the disadvantage that the motion of the air through the tube lessens the chance of particles adhering to the metal. Accordingly it was sought to demonstrate the effect by another method. Simultaneously with the exposure of the specimens represented by Curve B. in Fig. 23 (and immediately adjacent to them), three specimens were suspended inside a muslin “cage.”<sup>58</sup> The arrangement was such that the specimens were entirely surrounded by a single thickness of muslin, at a distance of several inches. The “cage” was only opened when necessitated by the periodical weighing of specimens. The somewhat extraordinary result then emerged that the *rusting of the specimens*

<sup>55</sup> See contribution by Dr. Simpson to the discussion on the First Report, *loc. cit.*, p. 912. Also J. S. Owens, *Proc. Roy. Soc., A*, 1926, 110.

<sup>56</sup> See Cohen and Ruston's “Smoke: A Study of Town Air” (Arnold). Shaw and Owens' “Smoke Problem of Great Cities” (Constable).

<sup>57</sup> In contradistinction to this result, it is of interest to recall that filtering the air is without influence upon the tarnishing of copper. See First Report, *loc. cit.*, p. 895.

<sup>58</sup> These experiments were started on January 30th, 1925.

*behind the muslin was entirely inhibited*, so that at the end of period W<sup>59</sup> they were apparently as bright as when first exposed, whilst the unscreened specimens had rusted in the manner already described. Although visibly unaffected the protected specimens increased slightly in weight during exposure, and their weight-increments are plotted in Fig. 23 (Curve A).

The disposition of the curve for the normally exposed specimens may now be explained. Rusting is due to the precipitation of solid particles from the atmosphere. Each particle is associated with sufficient adsorbed moisture or adsorbed acid to account for the attack upon the metal in the immediate vicinity, and no further. At first, when the whole area of the specimen is available for attack, the resulting weight-increment is relatively large, but the rate of change slows down as the available area becomes less. The falling off in the rate of attack is clearly due to fundamentally different causes from those which have obtained in any of the non-ferrous examples, and any resemblance in the curves is therefore purely superficial. So far from being "protected" in the ordinary sense, the surface of the metal at the end of Period W is potentially in an extremely active condition. This, however, will be discussed later.

**(c) Behaviour of Iron in Atmosphere Saturated with Water-Vapour ("Dew-point" Conditions), but Practically Free from Suspended Solid Particles.**

The specimens from which the curve of Fig. 24 was obtained were suspended on a wooden frame (approximately 2 ft. sq.) surrounded by muslin;

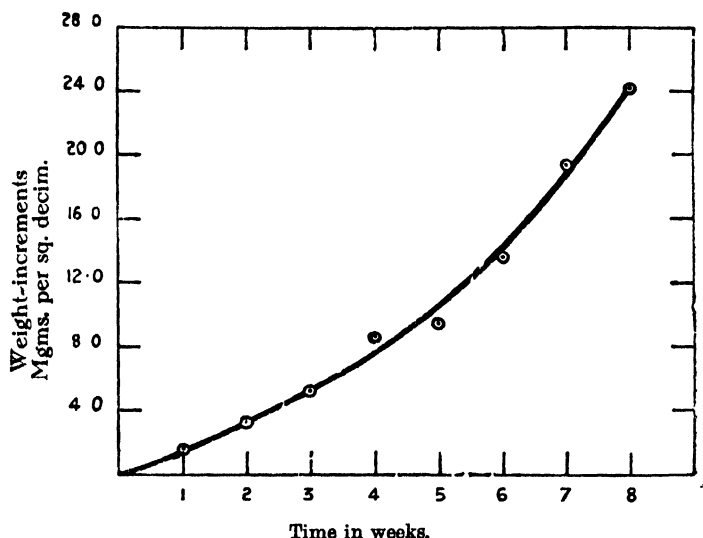


Fig. 24.—Rusting of iron in highly-humid atmosphere ("dew-point conditions") practically free from suspended solid particles.

this was placed in a large earthenware vat containing a layer of water, into which the lower part of the muslin dipped. The whole was covered by a glass plate and exposed to conditions away from artificial heating, so that

<sup>59</sup> Subsequent results, obtained *after passing through Period W* are discussed later—(e), p. 164.

diurnal fluctuations in temperature would undoubtedly result in the precipitation of moisture. The stand carried 16 specimens of which two were removed weekly and replaced by two others. Fig. 24 represents the mean total weight-increments for each week during 8 weeks' exposure. It will be seen that the curve is fundamentally different from that discussed under the previous heading (Fig. 23). As would be expected from the virtual absence of solid particles the attack is relatively slow at first, but accelerates later, owing no doubt to electro-chemical action rendered possible by the presence of a film of moisture. The relative purity of this moisture film presumably keeps down the rate of acceleration and, under the conditions of the experiments, a longer time of exposure would have been preferable; nevertheless the curve is sufficiently advanced to bring out the effect quite clearly.

#### (d) Behaviour of Iron in Indoor Atmosphere of High Relative Humidity.

The newer tests described below were carried out in atmosphere Type 1 during Period S. The (approximate) mean relative humidity during this period is 68 per cent., as compared with 43 per cent. for Period W. Suspended solid matter is most probably smaller in total amount, and is certainly less active in character, than that which obtains during Period W.

*Case 1. The iron is initially free from rust.*—This will be recognised as an intermediate case between (b) and (c) above, both in respect to the relative humidity of the atmosphere and also its content of active solid particles. It would be expected, therefore, that the effects upon a clean iron surface would be intermediate in type between those observed in the examples already given; this is borne out by experiment. Thus, in one season's observations the curve was slightly concave about the vertical axis (*i.e.* tending to follow Fig. 24), whilst in another the type of Fig. 23 was followed—with, however, an intensity of attack only half that during period W (0.6 as compared with 1.2 mg. per sq. dm. per 100 days). In the latter case, clearly, the observed effect was still due to active solid particles only, and the increased humidity was without influence during the period of the test.<sup>60</sup>

*Case 2. The iron is initially covered with dry rust.*—Previous considerations have shown that the function of suspended solid particles is the initiation of rusting, whilst the function of water-vapour (when present in sufficiently high concentration) is to supply the necessary moisture for the acceleration of this primary attack. The acceleration is effected by the juxtaposition, at each rust spot, of iron, rust, water, and oxygen. The presence of liquid water under conditions above the dew-point is accounted for in two ways: (1) the hygroscopic character of the "rust-spot," due both to the presence of the initiating "solid particle," and to the rust itself; (2) the increase in the concentration of atmospheric water-vapour above a certain critical value. If this concentration is not reached, a curve of the type of Fig. 23 is obtained. If it is reached and the surface of the iron is initially clean, the rate of rusting will still depend upon the rate at which solid particles can be precipitated upon the surface, and this may be quite

<sup>60</sup> In the light of results which immediately follow it would seem that the *acceleration of the curve from the start, above the dew-point, depends upon the precipitation of active solid particles in conjunction with, at the outset, a sufficiently high humidity.* The "critical humidity" necessary for this purpose appears to be distinctly higher in the early stages, when the rust centres are widely separated, than later on when the specimen is almost entirely covered with rust.

slow. (It seems probable indeed that they are not precipitated so fast when the humidity is high.) An interesting question arises as to what will happen if a surface already covered with rust (by the first of the processes considered) is presented to an atmosphere of approximately the critical humidity. Clearly this state of affairs is reached when specimens which have been exposed during "Period W," emerge into "Period S." The answer was at first supplied with unexpected and somewhat startling emphasis. Thus in the tests represented in Fig. 23, the mean weight-increment was

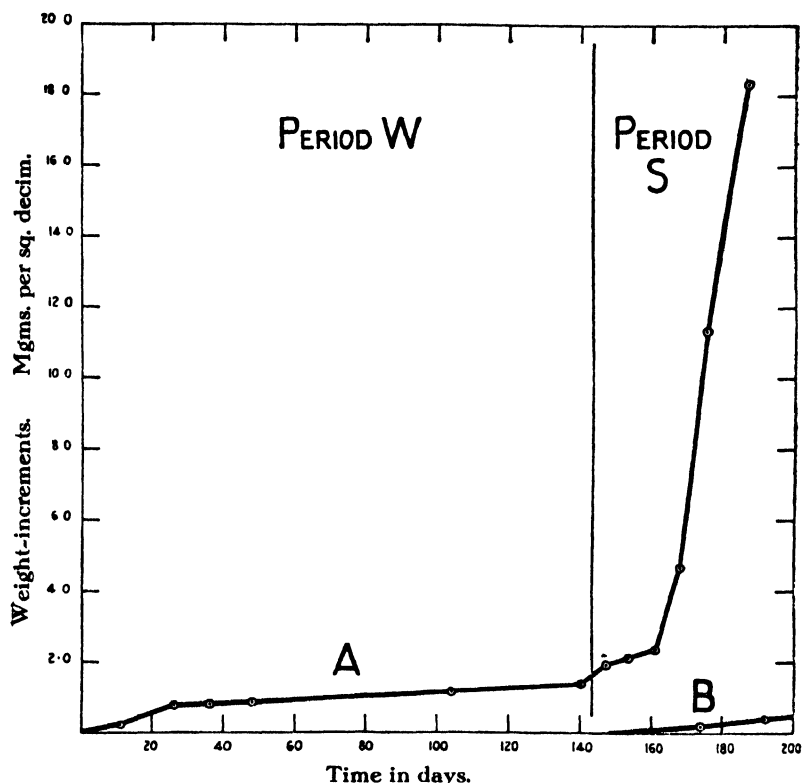


Fig. 25.—A—Effect of increase in atmospheric humidity (Period S) upon iron which has already rusted in a relatively dry atmosphere (Period W).  
B—Intrinsic effect of the more humid conditions upon freshly cleaned iron.

determined practically at the end of Period W (*i.e.* 92 days); it was then 2.2 mg. per sq. dm. No other determination was made until a further 67 days had elapsed, *i.e.* well within Period S; the weight-increment was then found to have the astonishing value of 48.5 mg. per sq. dm.<sup>61</sup>

This result was of such interest that it was decided, at the next opportunity, to trace the behaviour of the metal systematically during the transition period. The result is shown in Fig. 25, Curve A. Again the vertical line indicates approximately the position of change from Period W to Period S. (The values plotted are the means of figures obtained from six

<sup>61</sup> In Fig. 23, this corresponds to an ordinate (at 159 days) more than 12 times the total height of the diagram.

specimens, each of which would have yielded the same type of curve.) The almost immediate effect of entering the more humid period is now apparent, whilst the extraordinary acceleration is brought out clearly. Additional point is given to this result by consideration of the effect of the same atmosphere upon freshly cleaned specimens, as shown by Curve B in Fig. 25.

**(e) Formation of an Invisible Protective Oxide Film on Iron by Exposure to Air (Free from Suspended Solid Particles).**

The inhibition of rusting by the screening of specimens behind muslin has already been described; it will be recalled that specimens exposed in this way during Period W showed no visible alteration at the end of 92 days, during which time normally exposed duplicates had become covered with rust. It remains now to add that the altered hygrometric conditions consequent upon emerging into Period S, which have been seen to produce

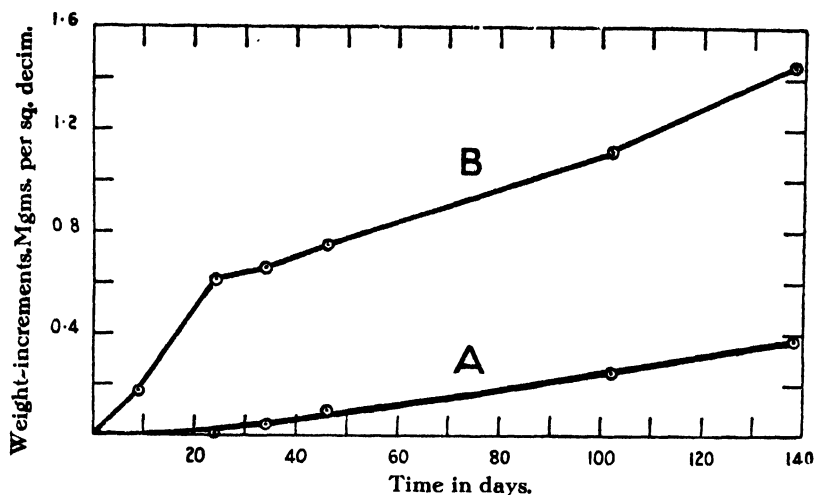


Fig. 26.—Relative behaviour on exposure to room atmosphere of A, iron which has been previously exposed for 11 months behind muslin (without rusting), and B, freshly-cleaned iron.

extraordinary effects upon rusted specimens and relatively slight effects upon those which have been freshly cleaned, were *still without any visible effect upon specimens screened behind muslin*. Neither, as will be seen by reference to Fig. 23, was there any appreciable alteration gravimetrically; the very small weight-increment already recorded had merely increased at almost exactly the same rate; the total increment at 159 days was 0.2 mg. per sq. dm. On the other hand, as already noted, the total weight-increment suffered by unprotected specimens was then 48.5 mg. per sq. dm.<sup>62</sup>

After 314 days' exposure behind the muslin, one of the specimens (still apparently unaltered) was withdrawn and exposed in the ordinary way, together with freshly-cleaned specimens. This was done early in Period W, so that the atmospheric conditions coincided exactly with those discussed under (c) above. The interesting result then emerged that *for a time the old specimen still preserved its brightness, whilst the rusting of the new ones*

<sup>62</sup> At this stage the disparity was increasing rapidly and, a little later, rust was actually falling away from the unprotected specimens, thus ruling out any further determinations of weight-increment.

*proceeded in the usual way.* Later, tiny specks of rust appeared, but the subsequent course of attack was then quite different from that which obtained in other cases, and consisted in an intensification of existing rust-spots rather than in the formation of new ones. From the weight-increments plotted in Fig. 26 the increasing rate of attack upon the pre-exposed specimen will be noted, in contradistinction to the falling-off in the attack upon the normal specimens. At the same time the relatively large disparity in the ordinates of the two curves confirms the suggestion that a definite degree of protection has been conferred by previous exposure. Apart from the actual breakdown of the film in the present instance, there is an obvious analogy with results already recorded for copper (p. 130) and for lead (p. 158). Although the nature of the attack has differed in each case, the resistance to this attack has undoubtedly originated in a common factor throughout, namely the formation of a film of oxide during previous exposure of the metal to uncontaminated conditions. Incidentally, the results would appear to have some bearing upon the wider phenomena of passivity.<sup>63</sup>

Finally, it may be observed that the local acceleration in the rate of attack upon the protected specimen is quite in harmony with the view that the protection is due to the formation of an invisible oxide film. At any rust-spot conditions are favourable for an "oxygen concentration cell," the underlying metal tending to become anodic. When, however, the rust is formed by the perforation of an initially-continuous oxide film at any point, clearly the ennoblement of the surrounding cathodic area will then accentuate any electrochemical effect, and hence lead to increased attack.

#### (f) Influence of Purity of Metal upon Rate of Rusting.

In the bulk of the tests described above specimens representing each of the following materials have been included:—

(1) *Ordinary Ingot Iron* (cold-rolled, close-annealed), as used in the earlier tests.

(2) *Electrolytic Iron*.<sup>64</sup> *Analysis*: Carbon, 0.04 per cent.; Mn, Si, S, P, Ni, Cr (total), 0.167 per cent.; Iron (by difference), 99.833 per cent.

(3) "*Armco*" *Ingot Iron*.<sup>65</sup> 99.84 per cent. Iron.

(4) *Spring Steel*. 0.5 per cent Carbon.

The ordinary ingot iron, only, was exposed to dew-point conditions. So far as conditions above the dew-point are concerned, it can be said quite definitely that the influence of purity and of composition (within the limits shown above) is nil. Specimens representing all materials have been exposed on various occasions and, even where comparatively wide differences have been displayed, the results have been definite only in the sense of showing that the composition of the metal had taken no part.

#### (g) Behaviour of Iron compared with that of Non-ferrous Materials.

In the First Report (*loc. cit.*, 886-890) results were quoted showing the relative behaviour of iron and non-ferrous metals in the atmosphere of the "basement" and the "tank-room," and also on exposure to the open air. Comparable results relating to exposure in a domestic kitchen are included in Section IV. of the present Report.

<sup>63</sup> Note for example the similarity in the effects produced upon copper by treatment with chromic acid (p. 120) and by exposure to air (p. 130).

<sup>64</sup> Kindly supplied by Dr. W. H. Hatfield, to whom the author is also indebted for a complete analysis and for a photomicrograph of the material.

<sup>65</sup> Presented by the Whitecross Company, Ltd., whose courtesy the author acknowledges.

*PART II.—OPEN-AIR EXPOSURE TESTS.***Introduction.**

In the First Report tests conducted upon specimens exposed completely to the open-air were described for copper, zinc, and brass (*loc. cit.*, pp. 975-80) and for iron (pp. 890-2). The results then discussed were confined to those yielded by measurement of the increase in weight of the specimen (up to 6 days), measurement of loss of reflectivity (various periods up to a maximum of little over 2 months), and ordinary visual inspection (up to the total period of just over 12 months at the time the report was written).

In the tests to be described (from which, however, iron has been excluded) the period during which the course of corrosion may be quantitatively followed has been extended by a system whereby the rain-water passing over specimens has been collected and analysed at convenient intervals. (Series A.) Ordinary loss of weight tests (supplemented by the analysis of corrosion products) are also described, representing a total period of exposure of over 4 years. (Series B.)

Square specimens of one decimeter edge and 3 mm. thickness have been employed throughout, and several types of surface condition have been investigated. (Series A.)

The exposure of the specimens has been conducted entirely at South Kensington, on the roof of the Royal School of Mines building (see First Report, *loc. cit.*, p. 855).<sup>66</sup>

*SERIES A.—COPPER, ZINC, AND BRASS.*

**Systematic Tests during Course of Exposure up to 100 weeks, Involving Estimation of Metal Removed by Rain. Computation of "Erosion," "Surrosion," and "Total Corrosion." Analysis of Corrosion Products.**

**Experimental.**

In the case of indoor exposure the changes taking place on the metal surface have been followed systematically by observation of the increase in weight of the specimen. On complete exposure to the open air, however, serious limitations are imposed. It is true that here, again, the action results in a scale which of itself must contribute to the weight of the specimen—indeed, measurements of weight-increase in the early stages have actually been carried out. (First Report, *loc. cit.*, 879.) But superimposed upon this effect—*i.e.* the *surrosion*<sup>67</sup> effect—the corrosion product must now be carried away to a greater or less extent through the agency of rain. To distinguish the latter from the former process a special term is clearly desirable, and fortunately an appropriate one is forthcoming in the word

<sup>66</sup> The task of extending the open-air tests to different localities—ultimately, it is hoped, to different climates—was entrusted by the Committee in March, 1925, to Mr. J. C. Hudson, M.Sc. To meet the special circumstances involved, Mr. Hudson has developed a method by which the electrical resistance of small coils is accurately determined before and after corrosion; a statement on this method in relation to the problem in hand was made by him in the discussion, recently, of a paper by Professor E. Wilson—*Proc. Physical Soc.*, 1926, 39, 23.

<sup>67</sup> J. Newton Friend, *Carnegie Scholarship Memoirs*, 1922, II, 1. See also, First Report, *loc. cit.*, 851.

*erosion*.<sup>68</sup> This expression will therefore be employed to denote that type of corrosion which results in the removal of material from the metal surface—as distinct from surrosion, which adds to it. Thus, atmospheric corrosion of the open-air type may be regarded as being made up of two components, surrosion and erosion respectively. It is evident, moreover, that the loss in weight of the specimen after prolonged exposure cannot be accepted as a criterion of the extent of the total alteration of the metal surface since it fails to distinguish between the two opposing factors of which it is the resultant.<sup>69</sup>

In the present tests (which were started on July 21st, 1922) an attempt has been made to obtain a direct measure of erosion by determining chemically the amount of metal removed in the rain-water falling over the specimen. This method has the advantage of enabling information to be obtained from time to time as to the course of erosion, without interfering in any way with the specimen itself. If, however, the loss in weight is determined at any given time, sufficient data are at once available to determine, from the total erosion, the extent of the surrosion with which it is accompanied. This was done for the whole series of specimens at 100 weeks' exposure.

*Specimens Employed in the Tests.*—Specimens (dimensions as given on p. 166) of copper, zinc, 70/30 and 60/40 brass were duplicated in each of the physical conditions enumerated in Table VIII.

*Method of Carrying Out the Tests.*—The general arrangement of the specimens during exposure will be clear from the photograph which was reproduced in Fig. 3 of the First Report. Specimens were suspended both vertically and horizontally, the rain being collected in suitable vessels and transferred to storage bottles for subsequent evaporation and analysis. In the method as carried out the solutions have been filtered previous to evaporation and the residue treated separately, with the object of differentiating between corrosion product in suspension and that in solution. Actually, however, the proportion held in suspension has been found to be extremely small, copper specimens yielding from 2 to 3 per cent. insoluble matter, brasses approximately 1 per cent., and zinc less than 1 per cent., showing that by far the greater amount of metal carried away in the rain-water is in a state of true solution. The figures given in Table VIII. incorporate in all cases the very small weights of metal found in the insoluble portions.

### Discussion of Results. (1)—“Erosion” Values (Metal Attacked, and Removed in Rain).

With reference to the results set out in Table VIII. the following comments may be offered.

*Influence of Surface “Skin” from Manufacture.*—Specimen No. 1 in each group was exposed in exactly the same surface conditions as received from the works, *i.e.* without polishing treatment of any kind. It is perhaps

<sup>68</sup> The author is aware that in corrosion literature the word is now generally used to signify the removal of metal by purely mechanical agencies. There appears, however, to be a very good case for using the terms surrosion and erosion in the way adopted in the present report, as originally suggested by Friend.

<sup>69</sup> It is true that in practice the specimen is scraped to remove the product of surrosion, but at best the method is unsatisfactory, on account of the virtual impossibility of effecting a clean separation of product and metal. The difficulty is especially great in the case of a material having a duplex structure, *e.g.* 60/40 brass, where one constituent may be attacked to a much greater extent than the other.

significant that the only really definite result is that yielded by copper, which shows an appreciably lower rate of erosion for the untreated specimen.

TABLE VIII.

COPPER, ZINC, 70/30 AND 60/40 BRASS: OPEN-AIR EXPOSURE (SOUTH KENSINGTON).  
"EROSION" VALUES: METAL IN RAIN-WATER COLLECTED FROM BENEATH SPECIMENS.

Reference No.	Physical Condition and Surface Condition. <sup>70</sup>	Vertical or Horizontal.	Period of Exposure, and Total Metal Found to Date (Grams). <sup>71</sup>					
			26 Weeks.		72 Weeks.		100 Weeks.	
<i>Copper</i>			Cu	Zn	Cu	Zn	Cu	Zn
1	H. W.	V.	.105		.252		.387	
2	" D.	"	.118		.300		.423	
3	" B.	"	.108		.288		.429	
4	A. D.	"	.109		.291		.427	
5	" B.	"	.107		.288		.428	
6	" D.	H.	.149		.381		.562	
7	" "	"	.151		.378		—	
<i>Zinc</i>								
1	H. W.	V.		.283		.771		1.195
2	" D.	"		.261		.693		1.095
3	" B.	"		.252		.746		1.149
4	A. D.	"		.261		.735		1.158
5	" B.	"		.295		.774		1.213
6	" D.	H.		.352		.996		1.392
<i>70/30 Brass</i>								
1	H. W.	V.	.020	.170	.047	.320	.077	.588
2	" D.	"	.024	.161	.060	.399	.142	.674
3	" B.	"	.022	.161	.056	.398	—	—
4	A. D.	"	.022	.116	.050	.371	.110	.611
5	" B.	"	.018	.167	.046	.427	.087	.714
6	" D.	H.	.033	.177	.101	.530	.156	.816
<i>60/40 Brass</i>								
1	H. W.	V.	.007	.171	.107	.410	.023	.587
2	" D.	"	.007	.160	.018	.448	.022	.655
3	" B.	"	.005	.120	.016	.338	.021	.596
4	A. D.	"	.010	.159	.026	.397	.027	.667
5	" B.	"	.004	.110	.016	.315	.017	.552
6	" D.	H.	.018	.200	.055	.542	.074	.824

<sup>70</sup> H. = Hard-rolled.

A. = Annealed.

W. = Surface as received from works (*i.e.* not polished).

D. = Surface polished, finishing with fine emery paper (Hubert, No. 1).

B. = Surface polished, finishing with "mops." (Bright "mirror" finish.)

<sup>71</sup> To convert to grams per sq. dm., values should be halved throughout.

There is some slight indication of a similar effect in the case of 70/30 brass, but with 60/40 brass and with zinc, no distinction whatever can be drawn.

*Influence of Physical Condition.*—(Nos. 2 to 5 in each group). In no case do the figures justify any conclusion being reached, either as between hard and soft specimens or those in the dull and bright condition respectively, except that any effects due to physical condition cannot have been appreciable under the conditions of the experiments. Indeed in the case of copper the values present an agreement which appears to be somewhat remarkable.

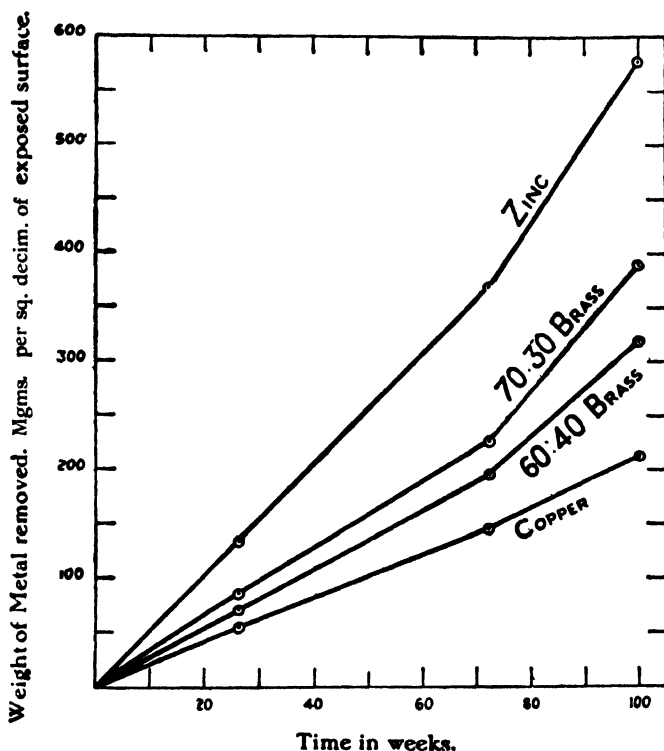


Fig. 27.—“Erosion” of copper, 70/30 brass, 60/40 brass, and zinc on exposure to the open air (South Kensington). Weight of metal removed in rain-water, in relation to period of exposure.

*Influence of Mode of Suspension.*—(Nos. 6 and 7, Copper; No. 6 in other groups). Specimens suspended horizontally have yielded appreciably higher results than those suspended vertically. The effect is most marked with 60/40 brass.

*Relative Erosion of Materials.*—*Relation between Erosion and Time.*—The average total values obtained from polished specimens at the end of 26, 72 and 100 weeks' exposure respectively, are plotted in Fig. 27. This serves both to show the relationship in behaviour among the different materials, and also the relationship between erosion and time in each case. It will be seen that the rate of erosion is excessively greater for zinc than for copper, while the brasses occupy an intermediate position.

Although, on account of fluctuations in atmospheric conditions, undue

significance cannot be attached to the disposition of the curves individually, it is noteworthy that the first two determined points fall almost exactly upon a straight line. In the case of copper the linear relationship is maintained, approximately, up to the last point at 100 weeks; in comparison, however, there is evidence of acceleration in the case of the other materials, more especially the brasses.

*"Dezincification" of the Brasses.*—The predominance of zinc in the corrosion products of brass is a quite general phenomenon to which the

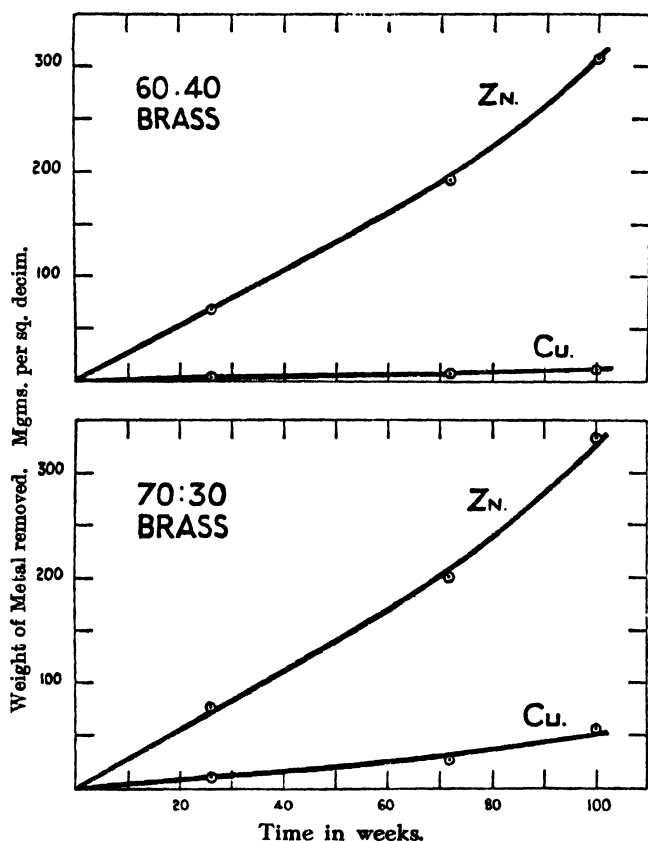


Fig. 28.—"Dezincification" of 70/30 and 60/40 brass on exposure to the open-air (South Kensington). Respective weights of copper and zinc removed in rain-water, in relation to period of exposure.

term dezincification is normally applied. In the case of sub-aqueous corrosion, however, the work of G. D. Bengough has shown that almost certainly the brass is attacked first as a whole, and that the appearance of excess of zinc in the product is due to a secondary reaction in which copper is re-deposited. Particular interest attaches to the values for the brasses in Table VIII., as showing the excessive preponderance of zinc over copper in the rain-water solutions. In Fig. 28 the values yielded by each constituent metal are plotted separately, for each alloy. It will be seen that although the total erosion is approximately the same, the extent of "dezincification"

TABLE IX  
Copper, Zinc, 70/30 and 60/40 Brass: Open-air Exposure (South Kensington).  
Corrosion Values after 100 Weeks.  
(All Values in Grams, as Actually Determined.)<sup>72</sup>

Reference No.	Condition of Specimen. (See Table VIII.)	Vertical or Horizontal.	"Erosion"—Metal Removed in Rain—"E." (From Table VIII.)	Weight of Specimen when Dis-mantled (after Washing and Drying.) W <sub>1</sub>	Initial Weight of Specimen. W <sub>2</sub>	Surrosion (in terms of metallic Portion of Residual Scale). S = W <sub>2</sub> + E - W <sub>1</sub>	Surrosion (in terms of Metallic Portion of Residual Scale). S' = S × Factor.	Total Corrosion of Specimens. C = E + S.	Loss in Weight after Scraping. (Grams.)	Loss in Weight. Total Corrosion.
<b>COPPER</b>										
1	H. W.	V.	0.387	273.2119	273.3245	0.274	S' = S (approx.)	0.661	—	—
2	H. D.	"	0.423	272.4680	272.6019	0.289	"	0.712	0.650	89.2 per cent.
3	H. B.	"	0.429	265.5438	265.7435	0.230	"	0.659	0.705	—
4	A. D.	"	0.427	264.2620	264.3865	0.303	"	0.730	0.596	—
5	A. B.	"	0.428	260.2695	260.3943	0.303	"	0.731	0.572	—
6	A. D.	H.	0.502	266.4105	266.6552	0.317	"	0.879	—	—
<b>70/30 BRASS</b>										
1	H. W.	V.	0.665	259.9096	260.0400	0.535	0.855	1.520	0.955	—
2	H. D.	"	0.816	259.8586	260.2240	0.451	0.722	1.538	—	—
3	H. B.	"	—	—	—	—	—	—	0.949	67.0 per cent.
4	A. D.	"	0.721	255.7452	256.0587	0.408	0.653	1.374	1.008	—
5	A. B.	"	0.801	253.2835	253.5773	0.507	0.812	1.613	1.119	—
6	A. D.	H.	0.972	254.0752	254.6164	0.431	0.690	1.662	—	—
<b>60/40 BRASS</b>										
1	H. W.	V.	0.610	255.4459	254.8863	1.170	S' = S (approx.)	1.780	—	—
2	H. D.	"	0.677	253.9584	253.4655	1.170	"	1.847	0.895	56.5 per cent.
3	H. B.	"	0.617	253.9856	253.6172	0.995	"	1.612	0.939	—
4	A. D.	"	0.694	249.6481	249.6126	0.730	"	1.424	—	—
5	A. B.	"	0.569	241.7377	241.3104	0.906	"	1.565	0.894	—
6	A. D.	H.	0.898	248.3920	248.7320	0.558	"	1.456	—	—
<b>ZINC</b>										
1	H. W.	V.	1.195	227.7311	228.7593	0.167	0.110	1.305	—	—
2	H. D.	"	1.095	223.5125	224.5652	0.042	0.027	1.122	—	—
3	H. B.	"	1.149	219.4332	220.4904	0.072	0.047	1.196	1.079	90.8 per cent.
4	A. D.	"	1.158	226.0313	227.0628	0.126	0.083	1.241	1.127	—
5	A. B.	"	1.213	220.0350	221.1350	0.113	0.075	1.288	1.085	—
6	A. D.	H.	1.392	227.9809	229.2482	0.125	0.082	1.474	—	—

<sup>72</sup> To convert to Grams per Sq. Dm., values should be halved throughout.

or "copper re-deposition" is very much greater for 60/40 brass than for 70/30.

An interesting sequel arises in connection with the "surrosion" results, to which reference will be made later.

**Discussion of Results. (2)—"Surrosion" Values (Metal Attacked, but remaining *in situ*). Computation of Surrosion. Analysis of Residual Corrosion-Products.**

When the specimens were dismantled at 100 weeks' exposure they were each washed many times with hot distilled water and the metal determined in the washings; the value obtained (actually quite small) was added to the erosion figures previously obtained. The object of this treatment was to obtain a figure for the maximum erosion, including not only metal already removed by rain, but also that still associated with the specimens in soluble form and therefore ready for such removal. The value for the total erosion ( $E$ ) is given in Table IX. After washing, the specimens were dried, thoroughly desiccated, and weighed. This weighing ( $W_2$ ) together with the initial weighing ( $W_1$ ) is also in Table IX. It will be seen that in no case is the loss in weight equal to the weight of metal actually removed. An interesting situation is presented by 60/40 brass, where, with the one exception of the horizontal specimen, the *final weight of the specimen is consistently greater than the initial weight*, in spite of the relatively large amount of metal which has been removed. The discrepancy is clearly due to the weight of the non-metallic portion of the scale which still adheres firmly to the underlying metal. It follows that an expression for the weight of material associated with the metal in this way is given by

$$S = W_2 + E - W_1,$$

where  $W_2$  is the final weight of the specimen,  $W_1$  the initial weight, and  $E$  the weight of metal carried away by rain.  $S$  is clearly the (net) surrosion of the specimen—calculated values of which are given in Table IX.

The abnormally high surrosion of 60/40 brass is perhaps significant, in view of the excessive "dezincification" displayed by this material (*vide supra*). In work published in 1922,<sup>73</sup> R. B. Abrams, after confirming the earlier conclusions of Bengough as to the initial mechanism of dezincification, showed that redeposition of copper does not take place unless there is some means of holding the dissolved metal in contact with brass, usually effected by the presence of some kind of "membrane." It is of interest to note that in the present instance the membrane is forthcoming in the relatively thick layer of "surrosion product."

The complete analysis of the product was carried out for each metal; the results are given in Table X. Generally no attempt was made to ascertain the solubility of the (powdered) product in water, and in most cases, in view of the smallness of the total amount and the very thorough washing which it received before removal, there was very little reason to suppose that any soluble matter was left. In the case of 60/40 brass, however, the possibility was suggested by the much larger amount of residual product; accordingly, a separate estimation was made, the results of which are given below.

<sup>73</sup> *Trans. Amer. Electrochem. Soc.*, 1922, 42, 39.

TABLE X.

COPPER, ZINC, 70/30 AND 60/40 BRASS. SERIES A. ANALYSIS OF RESIDUAL CORROSION PRODUCTS AFTER 100 WEEKS' EXPOSURE TO THE OPEN AIR (SOUTH KENSINGTON).

A. Analyses of the Products after drying at 105° C. Values as determined—metallic and non-metallic radicles, and matter insoluble in acids.

	Copper.	70/30 Brass.	60/40 Brass.		Zinc.
			As received.	Polished.	
Cu . . . . .	46.7	52.0	20.7	15.6	—
Zn . . . . .	—	5.5	21.9	29.6	36.2
Fe . . . . .	3.4	2.2	2.6	1.0	1.8
[CO <sub>2</sub> ] . . . . .	20.0	2.1	1.8	4.8	5.0
[SO <sub>4</sub> ] . . . . .	8.9	15.4	13.4	12.5	10.0
[S] . . . . .	2.9	4.4	10.8	10.8	5.8
[Cl] . . . . .	trace	trace	trace	trace	trace
Insol. Matter { Carbonaceous . . . . .	4.5	2.5	1.6	2.4	2.7
{ Siliceous . . . . .	3.3	3.3	2.7	1.3	1.0
[O], [OH] and } By difference . . . . .	10.3	12.6	24.5	22.0	37.5
combined H <sub>2</sub> O }					

B. Mean values of metallic and non-metallic radicles, excluding iron (with associated radicles <sup>74</sup>) and insoluble matter.

Cu . . . . .	54.6	57.7	17.9	—
Zn . . . . .	—	6.2	30.2	39.1
[CO <sub>2</sub> ] . . . . .	23.4	2.3	4.2	5.4
[SO <sub>4</sub> ] . . . . .	10.4	17.2	13.6	10.8
[S] . . . . .	3.4	4.9	11.5	6.2
[O], [OH], and } By difference . . . . .	8.2	11.7	22.6	38.5
combined H <sub>2</sub> O }				

C. Mean estimated values for principal constituents.

Carbonate . . . . .	48.2	4.8	8.7	11.2
Sulphate (anhydrous) . . . . .	17.3	28.9	22.7	18.1
Sulphide . . . . .	17.0	23.5	42.3	18.8
Oxide, hydroxide } By difference . . . . .	17.5	42.8	26.3	51.9
and combined H <sub>2</sub> O }				

Analysis of Residual Corrosion-product from 60/40 Brass.

<i>Aqueous Extract—</i>	Cu	trace	} 22.6 per cent.
	Zn	8.7	
	[SO <sub>4</sub> ]	13.9	
<i>Insoluble Residue—</i>	Cu	15.6	} 77.4 per cent.
	Zn	21.3	
	[CO <sub>2</sub> ]	4.8	
	[S]	10.8	
	[SO <sub>4</sub> ]	nil	
	[O], [OH], Comb., H <sub>2</sub> O. } Matter insol. in acids. }	24.9	

The presence of 22 per cent. of soluble matter (practically entirely, it may be noted, in the form of zinc sulphate), appears remarkable and testifies to the persistence with which soluble matter may be retained by the "membrane" in spite of drastic washing of the specimen.

<sup>74</sup> For the immediate purpose it is assumed that a given weight of iron accounts for a similar weight of [O] and [OH] radicles.

*Analysis of Residual Corrosion Products ("Surrosion Products") from the Whole Series.*<sup>75</sup>—Following upon the weighing ( $W_2$ ) of the (dried) specimens, they were scraped with a blunt tool to remove the residual corrosion product as completely as possible, with the minimum disturbance of underlying metal. The specimens were finally weighed (see below), and the collected products submitted to analysis. The results of the complete analyses in Table X. are given in three ways:—

A. Individual radicles, as actually determined, together with insoluble matter (carbonaceous and siliceous). This insoluble matter is obviously derived from external sources, and carried on to the specimens by wind; iron, which appears in all the analyses, must also be due to wind-borne contamination (largely, no doubt, from iron railings in close proximity) since all the materials were initially free from this element. The relatively large amount of material available in the case of 60/40 brass suggested a separate analysis of the product from the specimen exposed "as received"; apart from indicating a somewhat reduced dezincification, the result differs but very little from that given by polished specimens.

B. Mean values of essential radicles, excluding extraneous matter (insoluble, and rust). The figures for iron were eliminated by assuming a given weight of iron to account for a similar weight of [O] or [OH] radicles.

C. Mean values of main constituents. This gives the results in the form most convenient for comparison. Probably the most striking feature is the high content of sulphate and sulphide, particularly in the case of the brasses, with correspondingly low carbonate content. The production of sulphide appears to be especially favoured by 60/40 brass, as will be seen by the high figure of approximately 42 per cent. for the total sulphide in the product from this material.

### **Discussion of Results. (3)—Computation of Total Corrosion. Relation between Loss in Weight and Total Corrosion.**

*Computation of Total Corrosion.*—It is evident that an expression for the total corrosion of the specimens must include values for erosion and surrosion respectively. A difficulty arises, however, as to the form in which the separate values are expressed, since, in Table IX., E represents actual weight of metal removed, whilst S corresponds to the weight of non-metallic radicles in the residual corrosion product. The analyses, however, now enable a value to be obtained for the metal attacked, but remaining *in situ*. This has been done for each material and the results (S') are given in Table IX. Clearly, these figures are directly comparable with E, and therefore the sum of the two values represents the total weight of metal attacked, *i.e.*

$$C = E + S',$$

where C is the total corrosion. This value is given in Table IX. for the complete series.

*Relation between Loss of Weight and Total Corrosion.*—It is of interest to compare the final loss in weight of the scraped specimen with the value for complete corrosion obtained by the methods described above, bearing in mind that it is loss in weight which is usually accepted as the criterion of corrosion. The figures are given in Table IX.

It will be seen that with copper and zinc the difference between the two values is not very serious, the loss in weight accounting for approximately

<sup>75</sup> For methods of analyses, see Appendix.

90 per cent. of the total corrosion in each case. The discrepancy is comparatively large (67 per cent.) for 70/30 brass, and in the case of 60/40 brass reaches the seriously low figure of 56 per cent.

The explanation of this discrepancy is well brought out by observing the behaviour of 60/40 brass after the corrosion product has been removed, apparently completely. On polishing, and exposing to tarnishing conditions, the "original beta" constituent tarnishes extremely rapidly, owing to the fact that it now consists very largely of redeposited copper. If examined under the microscope after this treatment, the boundaries of the tarnished beta and the still bright alpha show up very clearly.<sup>76</sup> Moreover, the corroded beta constituent contains numerous cavities, offering lodgment for

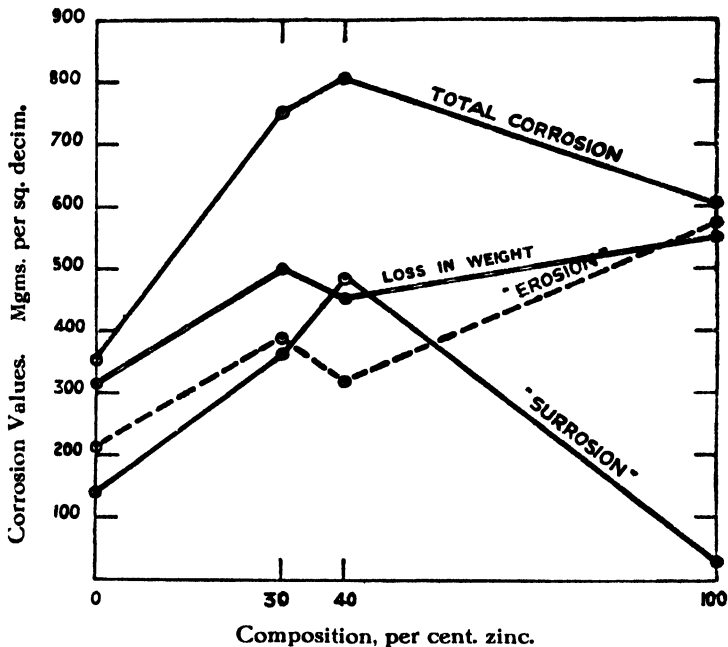


Fig. 29.—Corrosion Values of Copper, 70/30 brass, 60/40 brass, and zinc, after 100 weeks' exposure to the Open Air (South Kensington).

corrosion product, which thus fails to contribute to the observed loss in weight of the specimen.

- In Fig. 29 the several quantities which have been discussed are plotted against composition; it will be observed how very definitely erosion or surrosion, or loss in weight, fail, in themselves, to supply a true estimate, of the total attack upon the different materials, under conditions of complete exposure.

**SERIES B.—COPPER (VARIOUS GRADES), ZINC, AND BRASS (70/30 AND 60/40). 225 WEEKS' EXPOSURE.**

Specimens of this series, of which the various details are given in Table XII., were exposed on the roof of the Royal School of Mines building,

<sup>76</sup> Normally, under the same conditions, it is the copper constituent which tarnishes first. See p. 142

from July 21st, 1922, to Nov. 22nd, 1926, supported on a stand, a photograph of which was reproduced in Fig. 2 of the First Report. On dismantling they were dried, scraped with a blunt tool as before and the loss in weight was determined; the weight of product removed from each specimen was also obtained and the products were finally submitted to analysis. The procedure differed from that in Series A in that the rain-water solutions were not collected during exposure. Nevertheless the information gained from the more intensive earlier series was utilised in the interpretation of the later results, and in the computation of the approximate total corrosion.

*Analysis of Residual Corrosion Products.*—The results set out in Table XI. may be compared with the results already given for the shorter period of exposure in Series A (Table X.). It will be seen that whereas the sulphide content of the products from copper and 70/30 brass has fallen considerably, in the case of 60/40 brass and zinc it has remained about the same; hence the product from 60/40 brass is characterised by an even greater relative preponderance of sulphide.

TABLE XI.

COPPER, ZINC, 70/30 AND 60/40 BRASS. SERIES B. ANALYSES OF RESIDUAL CORROSION PRODUCTS AFTER 225 WEEKS' EXPOSURE TO THE OPEN AIR (SOUTH KENSINGTON).

A. Analyses of the products after drying at 105° C. Values as determined—metallic and non-metallic radicles, and matter insoluble in acids.

	Copper (H.C.).	70/30 Brass.	60/40 Brass.	Zinc (High Grade).
Cu . . . . .	62.7	50.4	10.5	—
Zn . . . . .	—	3.9	38.3	52.6
Fe . . . . .	1.0	2.0	1.3	2.3
[CO <sub>2</sub> ] . . . . .	2.9	3.8	2.0	2.5
[SO <sub>2</sub> ] . . . . .	17.4	15.5	10.1	7.7
[S] . . . . .	1.1	0.5	10.8	5.7
Insoluble matter . . . . .	5.0	7.8	4.9	4.0
[O], [OH], and } By combined H <sub>2</sub> O } difference .	9.9	16.1	22.1	25.2

B. Mean values of metallic and non-metallic radicles, excluding iron (with associated radicles) and insoluble matter.

Cu . . . . .	67.6	57.2	11.4	—
Zn . . . . .	—	4.4	41.4	57.5
[CO <sub>2</sub> ] . . . . .	3.1	4.3	2.2	2.7
[SO <sub>2</sub> ] . . . . .	18.7	17.5	10.9	8.4
[S] . . . . .	1.2	0.6	11.7	6.2
[O], [OH], and } By combined H <sub>2</sub> O } difference .	9.4	16.0	22.4	25.2

C. Mean estimated values for principal constituents.

Carbonate . . . . .	6.4	8.9	4.6	5.6
Sulphate (anhydrous) . . . . .	31.1	29.2	18.2	14.1
Sulphide . . . . .	6.0	3.0	39.9	18.6
Oxide, hydroxide } By and combined H <sub>2</sub> O } difference.	56.5	58.9	37.3	61.7

The sulphate content of the copper product having greatly increased, sulphate is now highest for that metal and lowest for zinc; also, it is much higher for 70/30 brass than for 60/40.

The carbonate content is low throughout, and there is little to choose in this respect among the materials. Generally the proportion of oxide or hydroxide is much higher than in Series A (*i.e.* the products are more basic); in both series it is highest for zinc.

*Determination of Loss in Weight of Specimen, and Computation of Total Corrosion.*—It should be explained that when the superincumbent corrosion product has been removed, there remains a *film* which appears to have entirely different properties, and which cannot usually be dislodged without removing underlying metal. The figures given for loss in weight do not necessarily include the weight of this film. For example, in the case of arsenical copper the film is exceedingly tenaceous and smooth and is virtually a part of the metal itself. It can only be removed by the use of a sharp instrument, with consequent abrasion of metal.

The values for approximate *total corrosion* given in Table XII. were obtained by applying the appropriate factor to the loss in weight figure (see Table IX.). As explained above the correction is not serious for copper and zinc, but is very appreciable for the brasses.

TABLE XII.

COPPER (VARIOUS COMPOSITIONS), 70/30 BRASS, 60/40 BRASS, AND ZINC. OPEN-AIR EXPOSURE (SOUTH KENSINGTON). LOSSES IN WEIGHT AND COMPUTED TOTAL CORROSION, AFTER 225 WEEKS.

Mark.	Description.	Losses in Weight.		Approximate Total Cor- rosion. <sup>77</sup> Grams. per Sq. Dm. <sup>78</sup>	Relative Corro- sion H.C. = 100.	
		Actual (Grams).	Grams. per Sq. Dm. <sup>78</sup>			
<i>Copper.</i>						
1 D/5	High conduc. Hard	1·768	·884	·889	·988	100
1 E/1	„ annealed	1·788	·894			
* 1 B/2	„ Hard	1·009	1·261	1·475	1·640	100
* 1 C/4	„ annealed	1·350	1·688			
2 D/4	Medium H.C. Hard	1·411	·705	·721	·802	81
2 E/2	„ annealed	1·477	·738			
4 D/3	0·75 per cent. Sn. Hard	1·463	·731	·679	·755	76
4 E/2	„ „ annealed	1·256	·628			
* N H/6	2·6 per cent. Ni. Hard	0·701	·877	·911	1·012	62
* N S/5	„ „ annealed	0·756	·945			
3 D/1	0·45 per cent. As. Hard	0·786	·393	·384	·427	43
3 E/3	„ „ annealed	0·752	·376			
<i>Brass.</i>						
70/6	70/30. Annealed	1·849	·924	1·380	140	
60/8	60/40 „	2·541	1·270	2·250	227	
<i>Zinc.</i>						
LH/1	High grade	2·920	1·460	1·379	1·530	155
Sl/4	Ordinary A	2·795	1·397			
S2/1	„ B	2·560	1·280			

<sup>77</sup> Values for "approximate total corrosion" are obtained from values for loss in weight by application of appropriate factor; see last column of Table IX. (Series A).

<sup>78</sup> Note that these figures (grams per sq. decim.) require to be doubled to be comparable with those in Table IX.

*Influence of Size of Specimen.*—In Table XII., specimens which are marked \* are of smaller area, each side being 0.4 sq. dm., as compared with 1.0 sq. dm. in other cases. Comparison of results from the first two "pairs" (all H.C. copper) brings out the much greater intensity of corrosion on the smaller specimens, loss in weight per unit area exceeding that of normal-sized specimens by about 65 per cent.

*Relative Behaviour of Materials: (1) Copper.*—In Table XII. the relative corrosion values of the materials are given, that of H.C. copper being taken as 100. Comparing the different varieties of copper, it is significant that corrosion is most severe on the purest material. The material which has resisted attack by far the best is arsenical copper, the corrosion value of which is only 43 per cent. that of H.C. copper. Nickel copper (2½ per cent. Ni) comes next, with a corrosion value of 62 per cent. In this connection it is of interest to recall the description of the visual results in the very early stages of exposure (First Report, *loc. cit.*, p. 875).—"With certain exceptions the appearances observed are practically the same for various grades of copper, the exceptions so far experienced being copper containing nickel (2.5 per cent.) and arsenic (0.45 per cent.). In each case a more rapid darkening of the original 'light-brown patina' is observed; whilst in the case of nickel-copper however the effect is comparatively slight, with arsenical-copper the greater rapidity of darkening is extremely pronounced." In connection with the optical results it was stated (*loc. cit.*, p. 878) that "among the copper specimens those of arsenical copper are always the first to have their reflectivity reduced beyond the limits of the optical bench." It would seem therefore that the formation of this initial film is actually a criterion of subsequent resistance.

The amount of corrosion product removed by scraping may be taken as indicating very approximately the "surrosion values" of the specimens. Relative values obtained in this way are given in the last column of Table XII., from which it will be seen that there is a rough parallel between surrosion and total corrosion; the explanation no doubt lies in the fact that through the accumulation of corrosion product, water is held for longer periods in contact with the metal.

*Relative Behaviour of Materials: (2) Brass and Zinc.*—It will be seen that the present results confirm those already recorded in Series A. and hence call for little further comment. Interest chiefly attaches to 60/40 brass which shows evidence of accelerated corrosion in the high value of 227 (H.C. Copper 100), actually by far the highest of the series.

The definite results yielded by copper of various compositions (above), suggest the desirability of obtaining comparable information upon zinc. In a new series of tests which is now being planned, it is hoped to amplify the work upon zinc, particularly from the point of view of influence of composition.

The author desires gratefully to acknowledge the invaluable encouragement and advice he has at all times received from Professor H. C. H. Carpenter, F.R.S., under whose general supervision the research is being conducted.

To Dr. R. S. Hutton and Dr. O. F. Hudson, of the British Non-Ferrous Metals Research Association, his best thanks are due for their sustained interest and readiness to help in every way. His colleague, Mr. J. C. Hudson, M.Sc., although fully occupied with the special investigation of another branch of the work, the results from which will be reported in due course, has also co-operated most helpfully.

It is again the author's pleasant duty to acknowledge the valuable services of Mr. L. Whitby (Research Assistant), and he would like especially to record his appreciation of Mr. Whitby's skill in connection with the analytical work.

Finally, the author desires to thank the Atmospheric Corrosion Committee, and the Council of the British Non-ferrous Metals Research Association for permission to publish the Report in its present form.

## APPENDIX.

### Methods used in Analysis of Corrosion Products.

The following notes do not attempt to give more than the briefest statement as to the methods ultimately relied upon for the estimation of the principal radicles.

*Copper*.—The ordinary "iodide method."

*Zinc*.—(a) *Relatively Large Amounts*.—Titration with potassium ferrocyanide.

(b) *Relatively Small Amounts*.—Precipitation as sulphide, reaction with iodine, and titration back with thiosulphate.

*Sulphide* [S].—Evolution as hydrogen sulphide, absorption in cadmium acetate solution, and titration with iodine and thiosulphate. It was found, however, that in the presence of excess of copper salt, hydrogen sulphide is not evolved on simple treatment with acid. The difficulty was overcome by the addition of stannous chloride in the evolution flask, thus maintaining copper in the cuprous condition. By this means a quantitative yield of hydrogen sulphide can be obtained, even when the amount of sulphide in the original mixture is exceedingly small.

*Carbonate* [CO<sub>2</sub>].—Evolution as CO<sub>2</sub> by means of phosphoric acid, and gravimetric absorption, after passing through acid potassium permanganate solution to remove any accompanying H<sub>2</sub>S.

*Sulphate* [SO<sub>4</sub>].—Precipitation as barium sulphate in the ordinary way, followed (for very small amounts) by centrifuging.

## SUMMARY.

The report is concerned with the behaviour of typical metals and alloys on exposure to the atmosphere; it is divided into two parts, dealing respectively with "indoor" and "open-air" exposure tests, the former including associated laboratory experiments. It is shown that conclusions which hold good for a given set of conditions do not necessarily apply when those conditions are changed; this is exemplified by the influence of "impurities" in copper. Indoors, under conditions such that only tarnishing has to be considered, a given element exercises an effect which is either negligible, or in simple proportion to the amount of element present. Exposed to the open air however, the same element may exert an effect out of all proportion to its concentration. It would appear that protection against indoor tarnishing should be sought by methods other than modification of composition alone; promising results have been obtained in connection with the formation of protective surface films.

The main conclusions relating to the two parts of the work are summarised below.

### Part I.—Indoor Exposure Tests and Laboratory Experiments.

#### Copper.

*Development and Inhibition of Tarnishing Phenomena*.—*Influence of Surface Condition*.—The intensity of attack, as measured by weight-increment per unit area, increases with the coarseness of the emery employed in abrasion.

*Influence of Chemical Cleaning*.—Treatment with solutions containing nitric acid is without appreciable influence upon the behaviour of the metal during subsequent exposure. Solutions containing chromic acid, on the other hand, produce a considerable degree of immunity from tarnishing; this immunity may be destroyed by treatment with ammonium chloride.

*Influence of Purity of Metal* upon rate of tarnishing appears to be negligible (although modifications of composition may have pronounced effects upon the corrosion of copper under conditions of complete exposure to the open air—*q.v.*).

*Influence of Sulphur Content of Atmosphere.*—The tarnishing of copper is initiated by atmospheric sulphur, in such form as to respond to the alkaline lead acetate test; the minimum concentration necessary for tarnishing, however, is extremely small (equivalent, approximately, to 1 volume of  $H_2S$  in 600 million volumes of air). Above this value tarnishing commences and proceeds at a rate proportional to the "reactive" sulphur content of the atmosphere.

When once a tarnish film is formed, increase in thickness follows accurately a parabolic relationship with time, though the atmospheric sulphur content may fluctuate within extremely wide limits; i.e., rate of tarnishing is determined by the conditions prevailing at the time of the first exposure.

*Composition of Tarnish Films, and Mechanism of their Formation.*—The sulphur (sulphide) content of tarnish films produced on copper in ordinary room air has not exceeded 15 per cent. Films consisting initially of pure sulphide, on exposure to ordinary room air, increase in thickness and continue through the same sequence of interference colours which they would have done if the original treatment had continued, but they do so mainly through absorption of oxygen. It is concluded that tarnish films consist essentially of isomorphous mixtures of oxide and sulphide, and that in the case of an initially-clean surface, under ordinary conditions of exposure, the surface is activated by the impingement of sulphur atoms, which enter into the formation of the first (mainly oxide) lattice; their relative distribution in this primary lattice then determines the rate of diffusion and the whole subsequent course of tarnishing.

There is reason to believe that if the first oxide lattice is completed before sulphur atoms can impinge (in the form and in the concentration in which they commonly occur in the atmosphere) their subsequent entry in any appreciable amount is prevented, and hence tarnishing is inhibited (see below).

*Formation of Protective Oxide Films at the Ordinary Temperature.*—When the content of atmospheric sulphur falls below the limit necessary for tarnishing, the formation of a thin film of oxide takes place, the progress of which has been followed gravimetrically. This film is unaffected by subsequent increase in the atmospheric sulphur content (within the usual limits), i.e. it is resistant to tarnishing.

*Formation of Protective Oxide Films at Temperatures above Normal.*—Whilst at the ordinary temperature there are two alternative types of film possible, i.e. the "tarnish film" and the "protective oxide film," according to the relative purity of the atmosphere, at higher temperatures the latter type is developed to the exclusion of the former. A curve has been plotted which connects the rate of film formation with temperature. There appears, however, to be a critical thickness of film necessary for protection to be afforded against subsequent tarnishing. (For one hour's heating this film is produced between  $55^\circ$  and  $75^\circ C.$ ) The evidence leads to the suggestion that the minimum thickness of film necessary for protection is such that the unit lattice of the oxide is completed for the whole of the surface.

*Protective Effects of Smoke Films.*—It has been found that close contact with smoke from cellulose produces a considerable degree of immunity from tarnishing on subsequent exposure.

## Zinc.

*Relation between Thickness of Film and Period of Exposure.*—The linear relationship between weight-increment and time, found in the earlier work, has been confirmed for relatively long periods of exposure; it holds true also in the early stages, with the probable exception, however, of the first day.

*Properties of Oxide Films Developed upon Zinc at the Ordinary Temperature.*—The linear relationship between weight-increment and time which characterises the oxidation of zinc at the ordinary temperature, leads to the conclusion

that the resulting film must have a granular structure, through the interstices of which gaseous diffusion of the atmosphere takes place. Direct evidence of this has now been obtained by examination under the microscope. Moreover, any colour effects should be due to diffraction and not to interference of light; this is confirmed by the regular appearance of a blue tint, without passage through the sequence of colours which is characteristic of interference.

### Brass.

*Relation between Weight Increment and Time.*—In an atmosphere of varying but mainly low relative humidity, both 70/30 and 60/40 brass for a considerable time simulate the behaviour of copper and yield curves which approximate very closely to the parabola. After more extended exposure however, they revert to the straight line which is characteristic of zinc. In a more humid atmosphere the resemblance to the behaviour of copper appears to disappear altogether.

*Effect of Atmospheric Exposure upon Microstructure (60/40 Brass).*—In an atmosphere of low relative humidity, containing traces of sulphur compounds characteristic of winter-time town air, the attack is at first chiefly directed upon the alpha constituent, which tarnishes in a similar manner to copper. Subsequently (and more rapidly the greater the humidity) the beta constituent is attacked, but the film is no longer "continuous" and takes the form of isolated pits, giving rise to an apparently duplex structure. It is suggested that this phenomenon is connected with the departure from the parabola to the straight line.

*Formation of Protective Oxide Films upon Brass.*—The film of oxide produced at the ordinary temperature by exposure to a relatively pure atmosphere, while affording considerable protection to copper, has relatively little effect upon the tarnishing of either 70/30 or 60/40 brass. Films produced at higher temperatures, however, exert a greater protective influence.

*Protection by means of Lanoline.*—In the case of brass exposed to a relatively humid atmosphere, a considerable degree of protection may be obtained by treatment with lanoline, combined with heat-treatment at 100°.

*Behaviour of Brass Compared with that of Copper and Zinc, in Several Types of Indoor Atmosphere.*—Results from tests extending over approximately 3½ years may be summarised as follows, the materials in each case being arranged in ascending order of the total corrosion which they have undergone.

A. Atmosphere of varying, but mainly low relative humidity.

(1) Copper, (2) 70/30 Brass, (3) 60/40 Brass, (4) Zinc.

The brasses tend to approach nearer to zinc with increasing time.

B. Atmosphere of varying, but mainly high relative humidity.

(1) Copper, (2) Zinc, (3) 60/40 Brass, (4) 70/30 Brass.

C. Domestic Kitchen.

(1) Copper, (2) Zinc, (3) 60/40 Brass, (4) 70/30 Brass.

The order is nominally the same as in B, but the attack on 70/30 brass is now very much greater than that on 60/40.

Analysis of corrosion products from specimens exposed in the domestic kitchen show that a certain amount of the attack is due to organic fatty acids; these appear to act preferentially upon zinc and give rise to their zinc salts in the corrosion products.

### Aluminium.

The formation of the primary film of oxide in the very early stages of exposure has been followed by careful gravimetric measurements which have led to the recognition of a weight-increment curve of an essentially different type from any of those previously obtained. Closely resembling a parabola at the outset, it quickly "flattens" toward the time axis, indicating an extremely rapid retardation in the rate of attack. The type of curve suggests that adsorption may play an essential part in the mechanism of oxidation in the present instance. In 10 or 14 days the primary film has practically ceased to thicken.

Assuming the film to consist of alumina, either anhydrous or hydrated, the weight-increment then corresponds to a thickness of the order of 100 Å.U. Subsequent increases in weight are probably due to the formation of cracks or fissures in the primary film.

### Lead.

The weight-increment curve is of the same type as that obtained for aluminium. The nearly flat portion of the curve is reached however in about 7 days and the weight-increment is then only a little more than half that which obtains for aluminium. As in the case of aluminium, the film is completely invisible.

It has been found that in the presence of traces of vapours from drying paint freshly-cleaned lead undergoes rapid oxidation and, in a week or so, becomes deep blue in colour. (Of all the metals examined, the effect is peculiar to lead.) If, however, the metal has been exposed for a sufficient length of time to the uncontaminated atmosphere, it is immune from such attack, owing no doubt to the formation of a protective film of oxide.

### Iron.

*Atmosphere of Relatively Low Humidity.*—In an ordinary room atmosphere of low relative humidity such as obtains under conditions of artificial heating, the process of rusting is controlled entirely by suspended solid impurities in the atmosphere. The weight-increment curve is concave about the time axis, *i.e.* the rate of attack falls off with increasing time. Rusting may be stopped entirely either by filtering the air, or by screening the specimen behind a single thickness of muslin.

During such time as the iron is exposed to an atmosphere screened from solid particles, it develops a protective film, in an analogous manner to other metals (*i.e.* copper and lead). On subsequent (normal) exposure this film definitely resists attack for a time, but then breaks down at certain points, following which the localised attack proceeds at an accelerating rate.

*Atmosphere of Relatively High Humidity* (such as may obtain in an ordinary room which is not artificially heated).—In the presence of suspended solid particles as before, and if the relative humidity is sufficiently high, the rate of attack accelerates from the start, owing to the deposition of particles and concomitant precipitation of moisture. (Rusting may still be prevented by screening behind muslin.) If iron, already covered with (dry) rust, is exposed to an atmosphere of the necessary relative humidity (actually not more than 70 per cent.), an extraordinary acceleration in the rate of attack at once takes place. These phenomena have been observed equally upon ingot iron of commercial quality, highly purified iron, and upon steel containing 0.5 per cent. C.

*Atmosphere Saturated with Water Vapour.*—Under conditions prevailing at the dew-point, rusting of the iron takes place in the absence of suspended solid particles. The rate of attack accelerates from the start, yielding a curve which is concave about the weight-axis.

## Part II. Open-Air Exposure Tests.

Intensive tests have been carried out upon specimens of copper, 70/30 brass, 60/40 brass and zinc, in various physical conditions. The rain-water has been collected from beneath these specimens and subjected to analysis at intervals. Information has thus been obtained concerning the weight of metal removed, in relation to the period of exposure. For the whole of the time in the case of copper, and for the major part of the time in the case of other materials, a linear relationship was found. The order in which the materials were affected by this type of attack (*i.e.* "erosion," as defined in the text) was as follows: Zinc, 70/30, 60/40, copper. In the case of the brasses there was excessive preponderance of zinc over copper in the soluble products.

From the weight of metal removed, and the initial and final weights of the specimen, a value was obtained for the "surrosion," represented by the residual products adhering to the specimens. Analyses of these products were carried out in all cases. The order of "surrosion" for the different materials was as follows: 60/40, 70/30, copper, zinc. Finally, by the summing of erosion and surrosion respectively, values were obtained representing the total corrosion of the specimens, in which respect the materials came out in the following *order of corrosibility*: 60/40, 70/30, zinc, copper.

Further tests, representing over four years' exposure, have been conducted upon various grades of copper, together with 70/30 brass, 60/40 brass, and zinc. The order of *resistance to corrosion* is given below, the figures indicating the approximate total corrosion, that of H.C. copper being taken as 100.

Copper with 0.45 per cent. arsenic . . . . .	43
Copper with 2.5 per cent. nickel . . . . .	61
Copper with 0.8 per cent. tin . . . . .	76
Ordinary copper . . . . .	81
H.C. copper . . . . .	100
70/30 brass . . . . .	140
Zinc . . . . .	155
60/40 brass . . . . .	227

In connection with the high resistance displayed by arsenical and nickel copper respectively, it was noted that within the first few days of exposure these materials, among the copper specimens, showed the most rapid loss of reflectivity.

**Dr. W. H. J. Vernon**, in presenting the report, emphasised the importance of the diffusion factor in atmospheric tarnishing. Thus, a specimen of copper might tarnish readily when suspended freely in a room, and yet remain bright indefinitely if enclosed in a bell-jar. Indeed, under such conditions it would slowly develop a protective oxide film.

He called attention to the following papers, which had been inadvertently omitted from the list given on p. 116.

*Gale, R. C.* "Note on temper colours." *J. Soc. Chem. Ind.*, 1924, **43**, 349T.

*Mason, C. W.* "Temper colours." *J. physical Chem.*, 1924, **28**, 1233.

*Turner, T.* "The oxidation of metals." *Met. Ind. (Lond.)*, 1924, **25**, 546.

**Mr. J. C. Hudson**, at the invitation of the President, said that the extension of the open air tests to different localities, for which purpose he was appointed about two years ago, had rendered it necessary to devise methods of measurement that are at once sufficiently wieldy to be applied on a large scale, and sufficiently sensitive to detect the changes produced within a reasonably short period. The problem now appeared to have been satisfactorily solved in two distinct ways; firstly, by the development of a method in which the change in the electrical resistance of a wire, brought about by corrosion, is accurately determined, secondly, by the application of the weight-increment method to specimens exposed outdoors, but sheltered from the rain in a Stevenson screen. Weight loss tests might also be carried out, although in this case, as Dr. Vernon had shown, caution would be necessary in interpreting the results. Preliminary investigations on experimental methods had been completed and, within a month or so, it was hoped to begin a systematic series of tests, by all three methods, on fifteen typical non-ferrous materials. Provision had been made for exposure

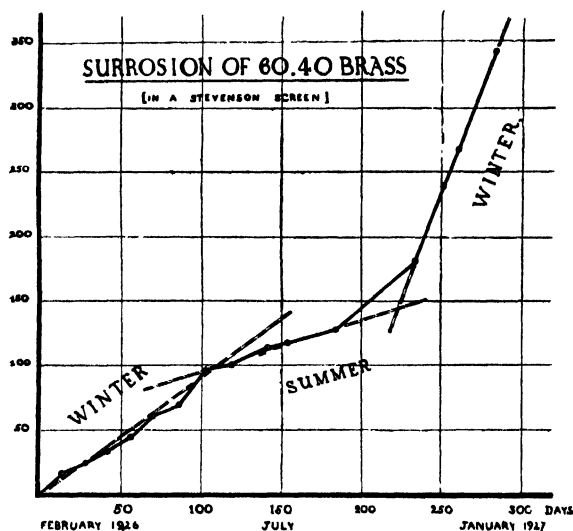
at five different stations in this country, which had been selected as typical of rural, suburban, urban, industrial, and marine atmospheres respectively.

In the course of this preparatory work, several points had emerged which bore on the present Report. For instance, there was a great difference in the rate of corrosion indoors and outdoors. Dr. Vernon showed that the corrosion of zinc was fifty times more intense on the roof than in the basement. He (Mr. Hudson) had observed even greater differences in the case of zinc coils exposed in the basement and in a Stevenson screen at the Royal Botanic Gardens, Regent's Park, respectively, as the following table of weight-increments after sixty days' exposure would show :—

SURROSION OF ZINC COILS IN DIFFERENT TYPES OF ATMOSPHERE.

Atmosphere.	Period of Exposure.	Weight Increment (Mgms. per dm <sup>2</sup> after 60 days).	Ratio of the Weight Increments.
1. Basement	Jan.-Feb., 1927.	1'4	1
2. Stevenson Screen at the	June-July, 1926.	22'1	16
3. Royal Botanic Gardens.	Nov.-Dec., 1926.	264	189

The surrosion of zinc was thus from 16 to 189 times greater outdoors than in the laboratory, and, also, there was a very marked difference in the



rate of corrosion outdoors during the winter and summer periods respectively. All metals corroded appreciably more during the winter, but the numerical ratio of the rates of attack during the two seasons was different for different materials; in the case of tests on twelve materials at the Royal Botanic Gardens, this ratio varied from 5.5 to 13 and, as a result, a radically different order of corrodibility was observed during

the two periods. Since climate was not only a function of season but also of locality, it followed that similar variations in the relative corrodibility of non-ferrous materials were to be expected in different regions of the earth's surface; they hoped that the coming field tests might bring some of these to light.

Dr. Vernon stated (on p. 142) that in the case of brass specimens exposed in the tank room, there appears to be definite evidence of acceleration of corrosion. The results of exposure tests on 60 : 40 brass specimens in a Stevenson screen, where the conditions were much more drastic, had confirmed this conclusion. The accompanying curve, in which weight-

increment was plotted against time, showed distinct evidence of an accelerated rate of attack, following a slight decrease in the rate, during the summer-period. It was difficult to decide whether this acceleration was due to a specific property of the corrosion product or to the advent of the more stringent conditions associated with winter; in all probability, the result was due to a combination of both factors. It was true that very marked condensation of moisture took place on the specimens in winter, owing to the increased humidity, but, on the other hand, this condensation appeared to be selective and to occur more readily on some materials than on others. It would seem that the relative deliquescence of the corrosion-product had an important influence on corrosion.

### DISCUSSION.

**Mr. A. E. Munby** as chairman of the Atmospheric Corrosion Research Committee expressed the appreciation of the Committee to the Society for the opportunity of the discussion of Dr. Vernon's work. He thought that results of ultimate practical value were emerging. He particularly referred to the films formed on metals at high temperatures which might lead to useful results.

**Professor H. C. H. Carpenter** emphasised the fact that Mr. Vernon in carrying out the work described in the report had had to work out his own methods. It was noteworthy that these methods should have given such consistent and satisfactory results. The method of weighing the specimens had been devised in conjunction with Professor Conrady. It was laborious, but the time spent on it was well spent. As the result of the adoption of those methods, Dr. Vernon had been able to establish some very important facts in connection with the formation of films. The most important and, he thought, vital of those was that the phenomena could be classified under three main heads.

Taking the co-ordinates—weight increments and time, the curves obtained were either a parabola, a straight line, or a curve which began as a parabola and then rapidly flattened towards the time axis. Copper gave the first, zinc the second, and aluminium the third. In the first case the film formation was regulated by diffusion through a solid envelope; in the second by gaseous diffusion only, while in the third it appeared to be dependent not on diffusion but on adsorption. Of these he gathered that the aluminium type of film was the most impervious, while the zinc film was the least impervious. From the point of view of the object with which this research had been undertaken the aluminium type of film was accordingly the best while that of zinc was the worst. So far Dr. Vernon had been examining types of films which were formed “naturally.” It would be an interesting development of this work to ascertain whether a film of the non-resistant type could be altered so as to render it more resistant by the particular set of conditions under which it was formed. Could, *e.g.*, the zinc film be rendered less pervious? Experiments in these directions seemed, he thought, to be called for and if successful would be most valuable.

The behaviour of the two brasses was, he thought, particularly interesting. The curve of weight-increment was characteristic of copper in the early stages and of zinc in the later stages. This would seem to indicate from the standpoint of resistance to tarnishing that the brasses were inferior

to copper—and speaking more generally that a pure metal was likely to be more resistant than an alloy.

The results obtained with iron stood rather in a class by themselves and were clearly influenced by the fact that the metal passed through two oxidation stages.

Dr. Vernon's Report constituted a most important record of scientific evidence bearing on the practical problems he hoped to solve. He (the speaker) thought the way was now opened for the application of those results to the problems in question.

**Dr. G. D. Bengough** said that to one studying the problem of corrosion in which the metal is immersed in water or neutral salt solutions, the report was of special interest in showing the widely different types of action which might be included under the word "corrosion." Not only might the controlling factors be different, but the whole mechanism might be different from the start—a fact that was, perhaps, not yet fully realised by the chemical world in general.

It might be of interest to summarise some of these differences, which have an important effect on the choice of experimental methods.

1. Dr. Vernon had shown that the nature of the metallic surface, whether abraded, ground on emery, or treated by certain kinds of chemicals had relatively little effect on the extent of corrosion, especially in the case of zinc, and good agreement between duplicate results was frequently obtained (*vide* First Report and Table IX., p. 171). In immersed corrosion experiments not only did different types of surface give widely different results, but closely agreeing duplicates were difficult to get even with the same type.

2. The close approximation to uniformity of action over the surface (apart from edges) in conditions which included exposure to rain was remarkable and quite different from what occurs in immersed corrosion. In Dr. Vernon's experiments there was practically no local action or pitting, which was the bugbear of immersion tests. Corrosion was strictly proportional to the surface area, a relation that did not always obtain in immersion tests according to the opinion of such eminent workers as Heyn and Seligman.

3. In the atmospheric corrosion tests of Dr. Vernon the nature of the corrosion product was usually of such a nature that continuous corrosion-time curves could be constructed because the action of weighing does not change its nature; this was an enormous advantage over immersed corrosion work in which such curves were urgently required but were much more difficult to obtain. The nature of the corrosion product and particularly the rate at which it allowed oxygen and sulphur compounds to reach the metallic surface was the main controlling factor influencing the speed of corrosion in atmospheric corrosion; but in immersed corrosion in conductivity water or very dilute salt solutions, although oxygen was necessary for corrosion, the controlling factor was the conductivity of the liquid. Oxygen did not penetrate to the seat of corrosion at all—a fact of great significance in differentiating the two types of action.

4. The nature of the film of the products of the action might evidently be widely different; for instance Dr. Vernon showed, on page 149, that for zinc a granular film showing diffraction colours might be obtained; on the other hand the cathodic films formed between the pits on immersed zinc were continuous and showed interference colours.

5. The initial portions of the time-corrosion curve for zinc were particularly interesting; that shown on page 136 appeared to cut the vertical axis

and probably really indicated a rapid initial action. On the other hand, zinc with immersed corrosion showed a retarded initial action in very dilute salt solutions.

6. A study of the curves for immersed corrosion of zinc specimens had recently been carried out in the Corrosion Research Laboratory of the D.S.I.R. They differed markedly from those published in this Report; they were more complicated and consisted of several branches which probably indicated different controlling factors.

It was clear that if the term "corrosion" were to be used to cover attacks both by the atmosphere and by dilute salt solutions, a very broad definition was required; indeed, it seemed probable that it could not be narrower than some such phrase as "corrosion is oxidation". It seemed clear that much further work—of a high order of accuracy such as had been reached in this Report—was required into the nature of both kinds of action.

**Mr. U. R. Evans** expressed his appreciation of the important results which had been achieved and of the sound policy by which the research had been guided. It was necessary to understand a disease before they could with confidence prescribe a cure; they might now fairly claim to understand the disease of atmospheric corrosion, and could thus approach the subject of mitigation or prevention. He hoped that this sensible policy would be adhered to by the Committee who gave guidance to the work.

With regard to Dr. Vernon's interpretation of his results he was, on most points, in complete accord with him. On a few minor issues, alternative explanations suggested themselves. The form of the oxidation-curve of aluminium (p. 152), for instance, could be explained most simply, if they remembered the curious change from the pervious to the impervious form of oxide, which occurred when aluminium was heated in air. Pilling and Bedworth,<sup>1</sup> working at 600° C., found that this change occurred quite suddenly, so that the oxide film suddenly ceased to thicken. Evidently at that high temperature the conversion, when once started at one point, speedily extend over the whole surface. But at ordinary temperature, the extension would be slow and oxidation would come to an end gradually, giving just the type of curve which Dr. Vernon had actually obtained (Fig. 19). No doubt Dr. Vernon was right in attributing the "subsidiary increases" (shown in Fig. 20) to cracking of the "primary film"; he had recently obtained evidence that the invisible oxide-film on iron also tends to thicken at ordinary temperature mainly by gas passing through cracks.

On page 133, Dr. Vernon had used the weight-increment of heated copper to calculate the thickness of the film produced; he had rightly designated the numbers so obtained by the word "approximate," since some oxide must have been present on the copper when the first weighing was performed; the metal had been ground in air and, although this original oxide was too discontinuous to be protective, its weight could not be neglected. He was inclined to think that the true thickness might considerably exceed the numbers given; optical considerations pointed in the same direction.

Dr. Vernon's work on sulphide and oxide films on copper was of great interest. He had often been puzzled by the fact that specimens of copper, originally tinted through exposure to hydrogen sulphide, continued to change in hue even when exposed to air containing practically no hydrogen

<sup>1</sup> *J. Inst. Met.*, 1923, 29, 529; especially pp. 573, 590.

sulphide. Probably the oxide formed below a sulphide-film was crystallographically continuous with the latter and was of the extended, pervious form which could not protect the copper from further attack; a similar pervious form of oxide occurred when hydrogen-charged copper was exposed to dissolved oxygen, the whole sequence of interference-tints, due to oxide films, being then obtained at ordinary temperatures.<sup>2</sup> On the other hand, when ordinary hydrogen-free copper was exposed to *dry* air free from hydrogen sulphide, the oxide film produced was much less pervious and before "visible" thickness had been reached, it was able to protect the copper below, not only from oxygen, but also from hydrogen sulphide—should that gas subsequently gain access to the metal. A mixture of oxygen and hydrogen sulphide, acting on freshly abraded copper, would cause a film sufficiently pervious to reach interference-tint thickness, firstly, because the film would be partly sulphide, which was naturally pervious and, secondly, because the removal of the hydrogen of the hydrogen sulphide by the oxygen gave just the conditions needed to ensure that the oxide also should be of the pervious variety.

He did not think that Dr. Vernon need apologise if his curves did not always conform to parabolic or linear forms. Any theory which considered both the physical and chemical stages of the film thickening process indicated that curves of these two types could only be expected if one of the two stages proceeded much less readily than the other. A rather more general equation (which, however, still neglected several complicating factors), was recently suggested by the speaker,<sup>3</sup> to connect the film-thickness,  $y$ , with the time  $t$ ; it might be written:

$$\frac{dy}{dt} = \frac{c_0 k_0 k_1}{k_0 + y k_1}$$

where  $k_0$  was a physical constant and  $k_1$  a chemical constant. This reduced to *parabolic* form when  $k_0$  was small compared with  $y k_1$ , and to *linear* form when  $y k_1$  was small compared with  $k_0$ ; but they might not infrequently expect to meet with curves which were neither linear nor parabolic. Under conditions where  $k_0$  and  $k_1$  were of the same order of magnitude, the resultant curve would be approximately *linear* when the thickness was *small* and *parabolic* when it was *large*. This was the state of affairs shown in the curve of Fig. 2 (page 125), and, whilst he did not deny the importance of the edge-effect emphasised by Dr. Vernon, he thought the main explanation of this type of curve was to be found in the way just suggested.

**Professor E. Wilson** said that as the result of Dr. Vernon's open-air exposure tests, high conductivity copper was much more seriously affected by corrosion than copper alloyed with small amounts of arsenic, nickel or tin. It was significant that exposure tests made on the roof of King's College, London,<sup>4</sup> showed a corresponding result in the case of aluminium. The specimens were in the form of wires 0.126 inch (0.32 cm.) diameter, and were tested at intervals for electrical resistance. If  $R_0$ ,  $R_t$  were the electrical resistances at the commencement and at time  $t$  during exposure respectively,  $\rho_0$ ,  $\rho_t$  the corresponding specific resistances,  $a_0$ ,  $a_t$  the corresponding cross-sectional areas, it followed that  $R_t/R_0 = \rho_t/\rho_0 \times a_0/a_t$ . In order to draw a comparison between a specimen of high-purity aluminium (25) and an aluminium alloy (7), the following figures were given:—

<sup>2</sup> *J. Chem. Soc.*, 1925, 127, 2484.

<sup>3</sup> "Corrosion of Metals," 1916, p. 14. (Arnold.)

<sup>4</sup> *J. Inst. Elect. Eng.*, 1925, 63, 1108; *Proc. Physical Soc.*, 1926, 39, 15.

	No.	Time of Exposure $t$ , years	Analysis.					$\rho_t/\rho_0$	$a_0/a_t$	$R_t/R_0$
			Si.	Fe.	Cu.	Ni.	Al.			
High-purity Aluminium alloy . .	25	{ 8 } { 23 }	0·14	0·31	—	—	99·55	{ 1·061 1·093 }	1·127 1·160	1·193 1·269
	7	24	0·37	0·25	0·05	0·75	98·58	1·091	1·025	1·119

It would be seen from the ratio  $a_0/a_t$  that for a given time  $t$  and length of specimen the loss of metal due to corrosion was much greater in the case of the high purity aluminium. It was pointed out by Mr. E. T. Painton<sup>6</sup> (The British Aluminium Co. Ltd.), that "an explanation of this discrepancy could be sought only in the particular specimen of pure aluminium which was not typical of the metal now used for electrical purposes. It would appear that present day high-purity aluminium had much greater immunity from the effects of atmospheric exposure; it would be of great scientific interest to know the reason of this change."

It was of interest to learn that Dr. Vernon had found sulphate in his corrosion products, as this confirmed the analysis of the corrosion on the King's College specimens; a similar remark applied to the entry of iron. The skin or membrane next to the metal was sufficiently compact to retain even soluble salts and the iron undoubtedly came from an outside source. As illustrating the different types of corrosion, Fig. 1 had been prepared by

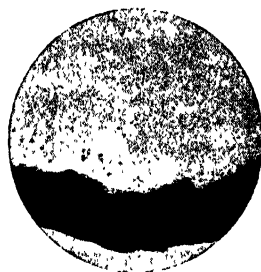


FIG. 1.—High-purity aluminium  
( $\times 30$ ).



FIG. 2.—Duralumin  
( $\times 30$ ).



FIG. 3.—Aluminium-copper  
( $\times 30$ ).

Mr. P. H. Busbridge from the high-purity aluminium after 23 years' exposure. The corrosion surrounded the aluminium in a more or less even layer. Fig. 2 was taken from a specimen of duralumin, the surface corrosion having been removed, and showed that the corrosion penetrates the metal almost radially in places; this presented a difficulty in estimating the total corrosion. The type shown in Fig. 3 which was obtained from another alloy containing 1·86 per cent. of copper again differed in that there were circumferential deposits within the metal itself.

As showing the effect of rain water it might be stated that the radial thickness of corrosion on the high-purity aluminium was the same after 23 years' exposure as it was after 8 years, although during this period there was a further loss of metal. The magnetic susceptibility of the corrosion product after 23 years was 1·6 fold the susceptibility after 8 years' exposure, which pointed to greater concentration.

<sup>6</sup> *Proc. Physical Soc.*, 1926, 39, 24 communicated remarks.

He suggested that the effects of corrosion upon the mechanical properties of the materials tested might with advantage be investigated. It was found, for example, that duralumin became exceedingly brittle on exposure. The effects of exposure upon structure was another important matter which might be considered.

**Professor T. Turner** said that the study of surface films was of the greatest importance in connection with corrosion. By taking a sheet of copper foil and heating it in air the metal became transparent. The thickness of the foil might be in the neighbourhood of  $\frac{1}{80000}$  of an inch, and such as could readily be purchased. The temperature of  $150^{\circ}$ - $200^{\circ}$  was suitable, varying with the time occupied. At first the colour was a light emerald green, and it gradually darkened in colour, passing through reds and purple. In such thin metal the two films, one on each side, met in the middle. Metals also became transparent when passing into solution, as shown in many metallic salts. These transparent films from copper were structureless when viewed under the microscope, and were solid solutions of oxide of copper in copper. Probably cupric oxide was formed, and dissolving in copper gave compositions of varying proportions, including the percentage composition of cuprous oxide. Oxide of iron (ferric oxide) appeared also to go into solution in iron to form a transparent film. In such cases the film increased in thickness with time and temperature. With aluminium there was no solid solution of oxide of aluminium in the metal and only a surface oxidation could be produced.

**Dr. R. S. Hutton** said that the report embodied the results of a splendidly sustained effort to increase our knowledge of the fundamental aspects of the subject; there was no doubt whatever that as its evidence became known not only would it have great influence on the further scientific study of corrosion problems, but practical applications of importance would arise.

Professor Carpenter had mentioned that in undertaking the general supervision of this investigation his chief object had been to secure the greatest possible freedom for Dr. Vernon in his work. The British Non-Ferrous Metals Research Association had fully appreciated this view and had tried to limit the interference in the work to a minimum. Probably without such safe-guarding it would have been impossible to maintain the work for so many years when there had necessarily been no immediate advantage to the industry which gave it the chief support.

Emphasis should be laid upon the fact that the report really recorded the discoveries of one man. Dr. Vernon had certainly the advantage of the stimulus of contact with Dr. G. D. Bengough and other workers in Professor Carpenter's laboratory, and had shown exceptional keenness in studying the vast literature of corrosion; but the patient and persistent research and the delicate and original methods of experimenting were entirely his own.

The careful study of the initial tarnish films on metals and the discovery of the protective effect of some of these we owed very largely to Dr. Vernon; his work fitted in most logically with that of other investigators in rather different fields, and to-day we appeared to be provided with a much sounder knowledge of the cause and of the progress of atmospheric corrosion than was available beforehand. The prospective application of this knowledge was most hopeful, as, with causes and progress made clear, the control and prevention could be studied with much better chances of success.

In this connection he asked Dr. Vernon if he considered other means

of strengthening or providing protective films likely to be of use in the application of non-ferrous metals to constructional purposes. In the first place S. E. Sheppard<sup>6</sup> described the treatment of copper and its alloys by alkaline persulphate solutions; although the passage was ambiguous, it appeared that the protection might be more easy with copper alloys than with copper itself, the reverse of what was found with heat treatment; this if confirmed was probably important.

The exceptional merits of aluminium oxide films for protective purposes were particularly promising where the composition of the alloy allowed for auto-regeneration of an oxide film at points where, by accidental abrasion or other means, the original oxide film had been broken down. The delicacy of "sprayed" or "calorised" surfaces, due to scaling, could perhaps be got over if alloys were used in which the aluminium formed one of the constituents. Some years ago in America "Calite" was suggested with this object, and in a different range of alloys both Dr. J. S. Dunn and Mr. R. Genders, working for the British Non-Ferrous Metals Research Association, had given evidence of the very low oxidations of brass containing a quite small percentage of aluminium. In such cases the breaking away of the surface film might be autogenously repaired by the oxidation of a further amount of the aluminium in the alloy.

**Dr. J. S. Owens** remarked that one very important thing had so far not been discussed, *viz.*, the connection established between the deposit of dust and the rusting of iron. Protection had been given to exposed plates by passing the air through a cotton wool filter and by suspending the plates in a muslin screen. It was, however, somewhat difficult to visualise the action of the muslin screen as the open meshes were of the order of 200 microns in diameter, while the particles of London haze were nearly all under 1 micron. Why therefore were they unable to pass through such large openings? The commencement of corrosion of exposed iron at specific foci also pointed towards the importance of dust deposition. He stated that the protection of the metal from dust might be approached in two different ways, either the metal might be covered to prevent access of the dust, or the air might be purified of the corrosivedust.

He drew attention to a statement on the top of page 163 in which Dr. Vernon remarked, with regard to the rate of deposit of solid particles upon a surface: "It seems probable indeed that they are not precipitated so fast when the humidity is high." Dr. Owens asked for the basis of this statement as he was of the opinion that the opposite was true; the viscosity of water vapour, which governed the rate of settlement, was approximately half that of air, and therefore the terminal velocity of dust in water vapour would be higher. Also in the case of hygroscopic particles condensation upon them would increase their effective mass and therefore their rate of settlement. He pointed out that while in the neighbourhood of the sea coast large numbers of salt crystals could be found in the air this was not the case further inland, and he attributed this to the deliquescence of the particles when the temperature fell and the relative humidity rose at night.

He thought that the question of a critical humidity might depend either upon the metal or upon the nature of the suspended matter, as different salts had different vapour pressures of deliquescence, but if the critical humidity were constant for different metals it would point towards the suspended matter as the governing factor, whereas if it varied with different

<sup>6</sup> *Nature*, 116, 608 (1925).

metals in the same atmosphere it would point towards the nature of the metal as the governing factor.

As bearing upon the effect of deposited dust on the metal, he suggested the exposure of two plates fixed back to back and exposed in a horizontal position, so that the upper surface of the top plate received the deposited dust whereas the lower surface of the bottom plate was more or less protected. It might be found in such a case that the weight increment of the two plates differed. He also drew attention to the necessity for keeping in mind changes in the degree of atmospheric pollution when corrosion experiments were made over long periods, and instanced the case of London where the deposit of sulphates had practically halved since 1915, which must have a considerable effect on the rate of corrosion.

**The President** remarked that the behaviour of metals of high purity in regard to corrosion was quite different from that of metals containing small quantities of impurity. The difference between a 99.2 per cent. and 99.6 per cent. metal was much less important than the difference between a 99.8 per cent. metal and one containing only faint traces of foreign elements. The spectrographically pure zinc prepared by the New Jersey Zinc Company, and the 99.95 per cent. aluminium, which was also manufactured, were extraordinarily inert towards mineral acids, being scarcely attacked after a week's immersion in hydrochloric acid. These metals remained very bright and untarnished on exposure to air, and it would be of interest to know how their behaviour compared quantitatively with that of the metals which had been examined so far.

It would be interesting to know what evidence Dr. Vernon had for the suggestion that the surface layer had the space lattice of copper oxide. According to the experiments of Langmuir and of Volmer the first thin layers formed at the surface of a metal were of irregular orientation, and it was not until a definite thickness had been reached that rearrangement to form a space lattice occurred.

**Professor R. C. Gale** suggested that the anomalous behaviour of lead when exposed to the vapours given off by drying paint might be due to the combined action of water vapour, carbonic acid gas and volatile fatty acids formed by the oxidation of the linseed oil in the paint. The presence of formic and acetic acids in the products of atmospheric oxidation of linseed oil had been shown by Mulder and others. The type of corrosion suggested was applied in an accentuated form in the process of converting lead to white lead by the so-called Dutch stack process.

The photomicrograph facing page 141 showed the great difference in the behaviour of the *alpha* and *beta* phases in 60/40 brass when exposed to air. It would be interesting to compare the behaviour of this alloy with that of a brass consisting entirely of the *beta* phase, since the appearance of the corrosion product was not unlike that formed on zinc, and possibly might give a weight-increment/time curve of similar type.

The inhibitory effect of a muslin screen on the "pitting" of steel might be due to the same cause as that found by Pasteur many years ago, *i.e.*, that solid particles such as bacteria floating in the air will not pass through small capillary channels. This fact was made use of unconsciously by the Sheffield cutler when he prevented the corrosion of his cutlery by wrapping it in paper which prevented the access of solid or liquid corrosive particles.

**Professor A. W. Porter** said that the protecting action of muslin was no doubt due to the prevention of air currents. A plate exposed in an ordinary room was subject to constant currents of air arising from differences

of temperature, and these brought with them fresh supplies of sulphur or other active materials. The muslin stopped these streams; the thin film of air clinging to the plate was rapidly exhausted and its sulphur content could only be replenished by diffusion. It did not seem likely that muslin of the mesh used would very materially reduce the chance of dust falling on the plate.

In regard to other matters in the report the most surprising fact was that consistent results could be obtained, at all, from experiments lasting over both summer and winter periods. The precise part which the sulphur played appeared to require further elucidation. Investigations with ordinary atmospheric air were of great importance in regard to the protection of metals from corrosion under ordinary conditions of exposure; but the scientific elucidation of the results obtained required experiments made with artificially "doped" air, the character of which could be maintained as uniform as possible throughout any one investigation.

The basis of the square-law for weight increment was rather difficult to understand. The equation suggested by Mr. Evans was still more obscure in its derivation. It might be mentioned that the curve in Fig. 2 was quite well fitted by  $W = A \log(a + t)$ . The reason for such an equation was as obscure as for the two others; it was however an equation which turned up in connection with many phenomena.

**Mr. A. Wolf** said it would be interesting to study the behaviour of a copper surface prepared by the familiar chemical reducing process of passing methyl alcohol over the strongly heated metal. He would expect such surfaces to be peculiarly susceptible to atmospheric corrosion in contradistinction to those which are protected by a film of oxide.

With regard to the experiments on the protective power of lanoline he pointed out decrease in reflectivity on prolonged exposure might be partly due to darkening of the protective film (owing to atmospheric oxidation) and to the adhesion of suspended matter in the air to the sticky surface; the same factors would also increase the weight increment. In his opinion, the removal of as much as possible of the lanoline by draining at 100° C. and wiping with cotton wool rendered the test too severe. The usual commercial procedure when using lanoline as a protective agent was to dip the article to be coated in a 10 per cent. solution of lanoline in a non-inflammable solvent such as trichlorethylene. The above method had been used with great success for the protection of aeroplane engines from atmospheric corrosion during transport and storage; it had been found that bright metallic surfaces treated in this manner would even resist corrosion when wholly or partly immersed in sea water during transport in the holds of ships.

The increase of fatty acid corrosion of brass with increase in zinc content on exposure of specimens to the atmosphere of a domestic kitchen was in accord with the experience that zinc was among the most easily corroded metals used in bearing metal alloys where the lubricant contained a large proportion of free fatty acid.

**Professor W. H. Merrett** said that whereas, on the one hand, corrosion films afforded protection to the metal, on the other hand they actually aided corrosion. Rolled copper sheets, strip and wire frequently become coated with a fine green patina of basic copper carbonate, especially when exposed to air near the sea. Some portions of the Dockyard roofs in this country, which were covered with copper, were to a great extent protected from further corrosion by this coating.

Concerning the use of lanoline, for the protection of brass exposed to

"dew-point" conditions, Professor Merrett said that until the war, linseed oil alone or linseed oil and white lead were generally used as a temporary measure for protecting machinery from corrosion; they were not efficient, since, as the oil dried, the layer which was left cracked considerably so that air and moisture could readily find their way through and corrode the metal beneath. Lanoline, however, did not dry and crack. Aero and other engines, recovered from torpedoed vessels, were found to be intact when they had been previously treated with lanoline, while those covered with other substances were corroded beyond redemption.

Professor Merrett said he would like to see more work done upon the corrosion of iron. There seemed to be considerable evidence to show that wrought iron was superior to mild steel against atmospheric and other types of corrosion.

Dr. Vernon dealt with the protection afforded by a film obtained by exposing copper to temperatures above the normal in air, and both Mr. Munby and Professor Desch had referred to the "red" copper produced by the Japanese. This could be obtained by casting copper on canvas under water and then exposing the cake to the action of steam. Such colouring lasted indefinitely; in fact, some specimens at the Royal School of Mines, which were at least fifty years old, still retained their fine red colour. Japanese experts were also able by suitable treatment, to produce protective patinas on copper, which might be made to show tints ranging from a rich golden sheen to chocolate. Professor Merrett stated that he had been able to reproduce some of these patinas by suitable chemical treatment of copper.

**Mr. S. Field and Mr. W. S. Patterson** (*communicated*): The results of the experiments upon zinc are of particular interest to us. The straight line relationship is now definitely established for indoor atmospheric exposure where the deposit accumulates. It will be of great interest to see if this is maintained in out-door exposure where the surrosion product is removed at irregular intervals by weathering. It would appear from Fig. 27 where the erosion (approx. 90 per cent. of the total corrosion) is plotted for out-door exposure that the corrosion of the zinc is accelerating, although over the first year the attack follows a straight line. It is curious that over three and a half years' indoor exposure the surrosion curve for zinc shows no seasonal fluctuations. Unquestionably there is considerable variation during this period in the acid sulphur content of the air and there can be no doubt that the surrosion deposit will contain sulphates. Is the attack of air upon zinc totally uninfluenced by sulphur compounds, or does the deposit once established prevent the access of such sulphur compounds to the metal, whilst permitting the access of oxygen?

We suggest tentatively, that the deposit, which is of a porous granular nature, may be acting as a filter; this appears to throw light on Dr. Vernon's results. If the scale functions in this way it is not neutral but really protective in that it eliminates a corrosive agent from the air. Dr. Vernon's suggestion of a critical humidity below which variations in water content do not appear to cause much effect upon the corrosion of zinc is a very important one and our own work confirms the suggestion. Dry air does not produce any measurable effect upon zinc, increasing the humidity to almost saturation has not increased the attack very considerably, but at complete saturation there is a large increase in the corrosion.

Dr. Vernon has shown, page 138, that in an unsaturated atmosphere the difference in the corrosion of highly polished and emiered zinc plates is practically nil. In a saturated atmosphere there is a difference. Dew is

deposited in small drops on the polished specimen and the usual pitting accompanying differential aeration occurs. In the emiered plates the attack takes place along the grooves cut by the emery and these are quickly made visible by the incrustation of deposit along them.

**Dr. L. H. Callendar** (*communicated*): The section dealing with aluminium interests me, as I have been engaged for the last six years on the study of the corrosion of this metal and its alloys. I have had some of this specially pure American metal, supplied to me by Dr. Vernon, analysed both spectroscopically and chemically. The spectroscopic analysis showed *only* Iron, Silicon, Copper, and Sodium. The chemical analysis gave Iron 0.017 per cent., Silicon 0.014 per cent., Copper 0.014 per cent., making the total impurities (with Sodium about 0.002 per cent.) less than 0.050 per cent.

Referring to the curves for the rate of oxidation of aluminium in air given on page 152, in some work I am shortly publishing, I have obtained some similar curves using a totally different method for measuring oxidation. This method, which is an adaptation and improvement on that described in a previous paper<sup>7</sup> and measures changes in potential of the aluminium surface and increases in the electrical resistance, appears to indicate both the rate of oxidation of the surface and the thickening of the oxide film. It is more sensitive than the weight-increment method as it indicates surface oxidation in a few minutes instead of only after several hours. Using the weight-increment method, as Dr. Vernon himself observes, the differences obtained are really due to differences in the relative freedom from oxide of the aluminium surface. That is to say, Dr. Vernon's curves for aluminium probably only represent the rate of thickening of the oxide film, the initial combination of oxygen with the metal being missed as this process will be mainly completed during the time taken (about half an hour), for the initial weighings. Potential curves I have obtained by the electrical method fall steeply at first showing the rapid covering of the metal with a molecular oxide film.

Some of the most interesting experiments in the paper are those in Section VII., in which Dr. Vernon shows that screening the air from dust prevents corrosion of iron. It is evident that the dust, sodium chloride, etc., settling on the metal tend to interfere with the formation of the normal oxide film and may even break it down where it has already formed. My experiments on Aluminium tend to indicate that in commerce substances deposited on the metal from the air probably determine the location of pits when the metal comes in contact with water. That this has not been generally recognised by previous investigators is because in their researches they have removed these anodic dust spots by cleaning, or polishing, or scraping the surface of their metal. This dust retained by the oxide film while it is thickening forms hundreds of anodic spots, the oxide film itself acting initially as the cathode of the corrosion cell and, under suitable conditions, any of these spots may develop into pits on the metal. In recent experiments I have found that minute emery particles embedded in aluminium increase the corrosion, frequently though not always forming starting points for pits on the metal. Anything that interferes with the even formation of the oxide film may thus be a cause of corrosion of the metal.

**Professor C. Benedicks** (*communicated*): The fact that zinc specimens gave the same weight-increment whether they possessed a dull emiered

<sup>7</sup> "Passivation and Scale Resistance in Relation to the Corrosion of Aluminium Alloys," *J. Inst. Met.*, 1925, 34, 57.

surface or a brightly polished one is interesting. Actually, in the first case, the true surface area must be much greater than in the other and, hence, a quicker rate of weight-increment would be expected. The explanation seems to be one of the two following. Either we may assume that the reaction takes place only on the ridges of the specimens. This would constitute a special case of the "edge effect" (p. 124) reduced to much smaller dimensions than otherwise. Or it may be that the zinc surface is attacked only at discrete points (pp. 139-140). The "point-surrosion" of a zinc surface in this respect seems to offer an analogy to the well-known oxidation of an aluminium surface in the presence of traces of mercury. Consequently, the surrosion on zinc would seem to be of a definite electrolytic character, due to some impurities, while, e.g., the "surrosion" of copper would appear as a more purely chemical process.

The conclusion as to the pre-determining influence exerted by an initially-formed film of sulphide or oxide are extremely interesting. The initial, though very thin layer, of sulphide may be said to exert precisely the same action as, in ordinary solutions, a "crystallisation centre"; the expression "germative layer" used by the author, seems a very appropriate one. The observations on lead (p. 158), lend valuable support to the conception of this selective action.

It is very interesting to find that under conditions permitting water condensation on the surface corrosion is most severe on the purest copper. He (Professor Benedicks) recently had to deal with a case of severe pitting on a copper plate, covered with a thick oxide layer. The conclusion he reached was that the corrosion was to a great extent due to the remarkably pure character of the electrolytic copper, the electrolytic potential being displaced in a less noble direction with increasing purity—at least with respect to cuprous oxide.

**Mr. Arthur J. G. Smout** (*communicated*): While the experimental work which has been carried out by Dr. Vernon on the problem of atmospheric corrosion is most interesting and of the highest scientific order, I hope that the practical aspect of this important subject will not be lost sight of, especially by those professions and branches of industry which are in daily contact with the problem.

Dr. Vernon has, during the past five years or so, devoted the whole of his time to this problem and it would, therefore, be exceedingly helpful to industrial workers if the author could at some near date summarise those aspects of the whole of his researches which have, perhaps, a more practical bearing on tarnishing and atmospheric corrosion. At the same time, I hold the view that the onus of application lies, not so much with the research worker, as some seem to think, but with the scientific and managerial staff of the works and industry concerned. Industry will benefit by this long and patient research only to the extent to which its scientific workers are prepared to apply the results to the betterment of their products.

In this connection I congratulate Dr. Vernon, not only on having studied the fundamental principles underlying the phenomena of tarnishing and atmospheric corrosion in such a manner that his work will stand the test of time, but on putting forward in this report many of his results in such a manner that they can be understood by persons industrially interested in the problems studied. Dr. Vernon has given definite leads in certain directions, and has made certain definite statements, all based on sound experimental work; it now remains for Industry to apply his suggestions.

The author's observation, contained in Part II. of the report, that modification of composition may result in greatly reduced corrosion when

various metals and alloys are exposed to the weather under ordinary conditions, can be fully substantiated by works experience.

The writer is connected with a firm of copper manufacturers who supply large quantities of copper for roofing and similar purposes in all parts of the world. Long experience has shown that for this purpose arsenical copper (c.f. British Engineering Standards Specification) containing 0.3 to 0.5 per cent. arsenic is the best form of copper to employ for this purpose and is much more suitable than H.C. copper of over 99.9 per cent. purity. The reason appears to be that a protective film is formed on this arsenical copper in the early days of its life by the action of the rain water. Cases are by no means uncommon where roofing contractors, especially in countries where rain is more or less infrequent, deliberately cause this film to be formed by washing down by some suitable means, in order to preserve their work from possible general deterioration in the course of time.

It is well known that the presence of arsenic in copper has a marked influence on the cuprous oxide eutectic, causing a "balling up" of the particles of oxide; the suggestion is made that this "balling up" of the oxide in arsenical copper may be the cause of the improved results obtained. The writer has reason (based on many works' observations) to believe that the cuprous oxide, which is present in manufactured copper, has a large bearing on the question of tarnish and atmospheric corrosion. Special methods are used by certain copper manufacturers to cast the cakes, which are subsequently rolled into sheet form, in such a manner that the cuprous oxide will neither be excessive nor unduly segregated, or concentrated, in any portion of the cake which will form part of the finished sheet or sheets. Methods are employed whereby that portion of the castings, in which segregation of cuprous oxide is likely to take place, can be subsequently removed as process scrap in the course of manufacture. Such material is technically known as "bloom copper." This concentration of cuprous oxide was noted by F. Johnson in 1925 in *Metal Industry*.

The writer's works experience shows also that all corrosion and tarnishing problems are materially affected by comparatively small modifications of composition of the material under observation, and that impurities play an important part, sometimes acting as a retarder and sometimes as an accelerating agent.

In this connection, it is now well known that ultra-chemically pure aluminium and zinc have properties totally different from those of the same metals as employed industrially, even when compared with the so-called high-grade varieties. It is, therefore, unfortunate that the author has not given detailed analyses of the various coppers, brasses, and types of zinc which he employed; this omission can be made good by supplying as an appendix to the paper full figures, including oxygen in the case of the coppers; the value of the report to subsequent workers, will be considerably enhanced.

**Dr. J. Newton Friend** (*communicated*): Dr. Vernon has explained the breaks in his aluminium curves by suggesting (p. 154) that when the primary film of oxide or other material on the surface of the metal exposed to corrosion has practically ceased to thicken, any further appreciable change takes place through the occurrence of cracks or fissures in the primary film. If such is the case one might perhaps expect a certain amount of pitting or localised corrosion to occur in the neighbourhood of the cracks, just as one finds pitting to occur in steel at cracks in the millscale when the metal has been exposed to corrosion without first de-scaling. It would be interesting

to learn if Dr. Vernon has observed any such tendency. In my own experiments, an aluminium bar exposed to the sea for four years is deeply pitted at various places, a typical pit, measured with a spherometer, being 2.35 mm. deep. The lead, zinc, tin, copper, and copper-alloy bars, on the other hand, are quite different.

Dr. Vernon's observation on the influence of dust upon the corrosion of iron in air at temperatures above the dew point is distinctly interesting, although quite in accordance with what one might expect. His statement that such small variations in the purity and composition as occurred between his specimens of iron and steel exerted a negligible influence upon his results is entirely in harmony with my own observations.

**Professor C. O. Bannister** (*communicated*): The report covers a very wide field of enquiry, an indication of the many lines of investigation it is necessary to follow up. Many of the results have a direct bearing on work in which the writer is personally interested. The fact that, in the case of zinc, the relationship between weight-increment and time, when exposed to the "unsaturated" type of atmosphere was found to be consistently linear, even for long periods is surprising, since similar tests carried out by the writer on galvanised sheets, showed a decided acceleration of corrosion after some months of exposure.

The different principles involved in the atmospheric corrosion of iron and of copper and bronze are of particular interest to all engaged in the examination of ancient specimens of metal objects, etc.; the new light now thrown by Dr. Vernon's reports on the methods of progress of corrosion in the case of the different metals will prove to be a most valuable aid in the correct interpretation of the changes which have been taking place during centuries.

In a recent book by the writer and H. Garland, on Ancient Egyptian Metallurgy it is suggested that iron and iron tools were known at much earlier periods than those generally accepted. It is interesting to note that the few very ancient specimens of iron tools which have resisted total decay have been those found in sheltered positions, protected largely from atmospheric dust as well as from moisture.

**H. Sutton and J. W. W. Willstrop** (Royal Aircraft Establishment) (*communicated*): The section on aluminium is closely related to some work they have been doing in their laboratory, and in which they have been isolating the oxide films on normal and treated aluminium sheets. The writers' experiments indicate that the film present on a normal sample of commercial aluminium sheet is of the order of 200 Å thickness, calculated from its weight, and assuming a density of 4. This result is in a fair agreement with Dr. Vernon's calculated thickness of the film produced by atmospheric oxidation. The thickness of the natural film may be expected to vary according to the nature of the surface.

**Dr. W. H. J. Vernon** (*in reply to the discussion*) expressed his gratification, both with the way in which the report had been received, and with the valuable discussion to which it had given rise. The difficulty of responding adequately to individual contributions would be appreciated, but he would endeavour to deal as far as was possible, or necessary, with the various points which had been raised. He appreciated the opening remarks of Mr. Munby as Chairman of the Atmospheric Corrosion Research Committee.

Professor Carpenter had very usefully surveyed the three main types of film that might be developed upon metal surfaces. He had pointed out the most serviceable of these, and had cogently enquired whether such a

type might not be stimulated artificially upon metals which normally gave rise to the less protective variety. With suitable modification of treatment, probably supplemented to some extent by modification of composition, the author saw no reason why that desideratum should not be attained, and he agreed that it was along such lines that future progress was likely to be made.

He heartily agreed with Dr. Bengough as to the widely different types of action which came under the heading of corrosion. The results obtained according as one was dealing with the metal-gas or the metal-liquid interface certainly provided marked contrasts, some of which were probably not unconnected with the molecular and ionic nature of the reactions in the two cases respectively. A more useful conception however, in particular cases, was that of the "controlling factor," which Dr. Bengough had mentioned. A good example of this was afforded by the consideration of duplicate results, in the tarnishing of copper and the rusting of iron respectively. In the first part of the Report tables of results corresponding to the various curves had been omitted through considerations of space. In the case of copper it could be said that duplicate experiments had always shown extremely close agreement, certainly much closer than the bulk of those given in Table IX. (Open Air Tests) to which Dr. Bengough had alluded. Here, however, the process was controlled entirely by the properties of the initially-formed film, which, in turn, depended upon the atmospheric (gaseous) conditions prevailing at the time of the first exposure; hence the agreement of duplicates was readily understood. In the case of iron, on the other hand, the degree of rusting of a given specimen depended upon the extent to which particles were precipitated upon the surface during the course of exposure, evidently a much more capricious factor; in this case duplicate results almost invariably shewed considerable divergences.

The differences between results obtained in atmospheric and immersed corrosion respectively, appeared to have very useful light thrown upon them by the contribution of Dr. Callendar in the present discussion. Thus, considering the case of aluminium, in the formation of the primary film it was evident that a large number of slight discontinuities or pin-holes in the film would affect the weight-increment but very slightly, whereas on immersion in a liquid the distribution of those pin-holes might determine the whole course of the attack. Under such circumstances it was evident that no two specimens could be expected to yield similar quantitative results.

The author fully agreed with Dr. Bengough as to the advantage afforded in atmospheric corrosion work by the great extent to which the effects could be followed by direct weighing. The high order of accuracy which Dr. Bengough and his associates were obtaining in their investigations into the genesis of immersed corrosion was attended with much greater difficulties, but their results would undoubtedly prove of far-reaching importance.

The 'alternative explanations' brought forward by Mr. Evans naturally called for serious consideration. Anything which would throw light on the oxidation curve obtained for aluminium and for lead was greatly to be welcomed, since there was real difficulty in interpreting this curve. The suggestion, however, that the oxide changed from a pervious to an impervious form during oxidation of the metal, seemed only to raise the question as to what was the mechanism of this change; the answer appeared to be equally obscure under ordinary temperature conditions. Of

greater help was Mr. Evans' view that oxidation might start from "points,"<sup>8</sup> the flattening of the curve then marking the stage at which the whole surface was covered with oxide. The author was particularly interested to note that his suggested explanation for the "subsequent" increments was confirmed by Mr. Evans' work on oxide films on iron.

The figures given on page 133 for the "approximate" thickness of oxide films upon copper were really only intended for comparing the thickness of the respective films, which purpose was served even though the individual figures were admittedly very approximate.

Mr. Evans' general equation was of great interest. It seemed, however, most significant that in practice one found the metal showing a most marked predilection to give *either* a straight line *or* a parabola; in the course of the present work truly intermediate types had not been encountered in the case of pure metals. The initial straight line given by copper specimens in the early stages of tarnishing, he believed, was to be explained on the lines suggested in the text; otherwise the "edge effect" would still have to be accounted for, whereas a consideration of this effect would lead one to expect exactly the sort of relationship which had been realised experimentally. It might be noted that an "intermediate" curve appeared to obtain in the case of the brasses, but here the work seemed strongly to suggest that the constituent metals were actually behaving as separate entities.

The results which Professor Wilson had quoted from his investigations on the electrical properties of wires as affected by prolonged atmospheric exposure were interesting, and he would await with interest any further development as to the effect of impurities on the atmospheric corrosion of aluminium. Of considerable interest was the evidence adduced by Mr. Busbridge as to the penetration of corrosion into the interior, in the case of the aluminium alloy. In reply to Professor Wilson's suggestion that the mechanical properties of the materials should have been tested, the author would point out that in the case of non-ferrous metals, mechanical tests were not sufficiently sensitive to detect changes due to atmospheric corrosion, within a reasonably short period of time.

Such experiments as those of Professor Turner on transparent films demonstrated directly what could only be inferred indirectly from interference colours, as to the transparent nature of the oxide films produced at the temperature stated. Touching the question, however, as to the particular oxide which was formed, he would point out that since the whole layer became transparent, including the intermediate film of unoxidised metal, there would appear to be a very close similarity between the crystalline structure of the oxide and that of the metal, a condition which, it would seem, could only be fulfilled in the case of cuprous oxide.

With regard to the work of Sheppard (mentioned by Dr. Hutton) on the action of potassium persulphate solutions on copper or brass, as originally described<sup>9</sup> the experiments showed that whereas on immersing a strip of the metal quickly in the solution it blackened readily and completely, if it were lowered slowly blackening either did not take place or was very patchy and imperfect, generally not more than a tarnish. From his own (admittedly limited) experience in repeating the experiment the author could confirm the "very patchy and imperfect" nature of the tarnish film so produced. Sheppard showed that the reactions involved were probably complex.

<sup>8</sup> A similar suggestion had been made by Professor Benedicks in connection with zinc.

<sup>9</sup> *Nature*, 1925, 116, 608.

Scientifically the observation quoted was undoubtedly of great interest, but it had not seemed to him to be sufficiently cognate to call for inclusion in the present report.

The great disparity between the size of the muslin mesh and the dimensions which Dr. Owens' important work had established for the solid particles in the atmosphere, was certainly puzzling. The author thought it was helpful to approach the matter in two ways: firstly considering the solid particles themselves, by regarding them as not stationary, but in a state of oscillation as presumably they would be in the air, whence the dimensions of the mesh necessary to trap them would be equivalent, not to the actual diameter of the particles, but to the distance representing the extent of their lateral movement; secondly, as pointed out by Mr. Wolf, by considering the muslin meshwork not as clean-cut holes, but as probably including small branch fibres projecting toward the centre of the mesh. In addition, the probability of a certain amount of capillary attraction between the solid particle and the material of the mesh, should also be borne in mind.

With regard to the influence of increasing humidity upon the rate of precipitation of solid particles, the author gladly accepted Dr. Owens' correction. This rendered the lesser intrinsic corrosivity of the more humid atmosphere all the more remarkable, and caused even greater importance to attach to the specific nature of the solid particles themselves during the summer and winter periods respectively.

The critical humidity mentioned by Dr. Owens certainly differed very greatly for different metals, probably most largely on account of differences in the vapour pressures of the respective corrosion products. At the same time the author fully agreed that hygroscopic particles settling from the air must play some part in determining the actual value of the critical humidity.

The President had raised a point of great interest in respect to the effect of impurities, a matter to which Mr. Smout had also referred. When one was dealing with the metal-gas interface, impurities in the metal appeared to play an unimportant part. Thus, in the experiments with aluminium the author had employed the 99.95 per cent. metal<sup>10</sup> referred to by the President, but with respect to the rate of film formation this had not differed appreciably from the metal of ordinary purity. He agreed, however, that when one came to deal with the metal-liquid interface—and more particularly with corrosion in acid solutions—the question of the last traces of impurities might become of great importance. Zinc afforded a good example of this, because whereas the spectroscopically pure metal displayed the excessively high resistance which the President had described, there was evidence that between this material and metal of ordinary purity there was a critical composition, equivalent to the merest trace of impurity, at which the metal dissolved with extreme rapidity.<sup>11</sup>

With regard to the space lattice of oxide films, Pilling and Bedworth<sup>12</sup> had shown in the case of thick films that these were definitely crystalline; they had published photo-micrographs of such films which bore close resemblance to ordinary metallic microstructures. It was evident that the crystalline structure must also hold true for much thinner films, which would

<sup>10</sup> See p. 150, also p. 195, contribution by Dr. Callendar.

<sup>11</sup> On the authority of Mr. Gilbert Rigg, late of the New Jersey Zinc Company; see H. C. Lancaster, *Trans. Faraday Soc.*, 1924, 19, 920. See also, T. D. Lynch, and F. G. Breyer, *Proc. Amer. Soc. Test Mat.*, 1924, 24, 762.

<sup>12</sup> *J. Inst. Metals*, 1923, 29, 558.

therefore be expected to possess a definite space lattice; in the case of copper (as noted in reply to Professor Turner) there were good reasons for believing that this was the space lattice of cuprous oxide. With progressive thinning of the film a stage must clearly be reached when the unit lattice of the oxide was *not* completed for the whole of the surface, *i.e.*, a state of irregular orientation, in harmony with the results of Langmuir and Volmer. This state of affairs had been envisaged by the author (p. 132), and it would appear that the metal was susceptible to tarnishing influences just when it was in this condition. When once there was a definite oxide space lattice over the whole surface, the surface would naturally take on the properties of the oxide as distinct from those of the metal, and one would expect a more or less well-defined break in properties as one approached the completely oxidised condition; it would be recalled that this sudden break had been experimentally realised.

The author had been greatly interested in Professor Gale's suggestion, endorsed by Mr. Wolf, with regard to the anomalous behaviour of lead. The possibility of traces of formic acid giving rise to the observed effects had been considered at the time; to test this lead strips had been suspended over formic acid solution. Only slight effects were produced in this way, however, less than those obtained by substituting turpentine<sup>13</sup> for formic acid, and very considerably less than those obtained in actual practice in the presence of vapours from drying paint (characterised by the "smell of paint"). Evidently there were other factors at work which so far had not been elucidated.

The author could not agree with Professor Porter that the inhibitory effect of a muslin screen upon rusting was due simply to the prevention of air currents. If that were so the tarnishing of copper should also be prevented. It was true that the rate of tarnishing was somewhat reduced by screening behind muslin, but tarnishing still went on and copper so exposed passed through the usual sequence of colour changes. On the other hand, iron specimens, similarly exposed, might be kept, apparently indefinitely, without rusting. Moreover, the rusting of iron could also be stopped by filtering the air, irrespective of the rate of flow; under such conditions however, the tarnishing of copper was not affected, and indeed proceeded at a rate which increased with increasing rate of flow of the air.

In connection with the tarnishing of copper, Professor Porter had expressed his surprise that consistent results should be possible over both winter and summer periods; Professor Porter's surprise, however, could not exceed that of the author when this remarkable fact was first observed. It was one which certainly called for explanation, but at the same time it indicated fairly clearly that the explanation was to be found in a specific property of the initial film.

Professor Porter, like Mr. Evans, differed from the author in the interpretation of the curve shown in Fig. 2, and in each case a different mathematical solution was proposed. While the author was glad that both equations had been included in the discussion, he could not refrain from deprecating undue reliance being placed upon an equation simply because it happened to fit a given curve. He considered that the test should be whether the equation agreed with the experimental facts, of which, after all, the weight-increment/time curve was only one. The simple parabolic

<sup>13</sup> Levy and Defries ("Action of Turpentine on Iron," *J. Soc. Chem. Ind.*, 1923, 42, 472T) point out the probability of acids of much higher molecular weight than formic or acetic acid being formed during the oxidation of turpentine, in presence of moisture.

equation ( $W^2 = Kt$ ) was capable of perfectly definite physical interpretation (see p. 124)<sup>14</sup> and, within the author's experience, was in agreement with the whole of the observed facts.

He hardly thought that the method of covering with lanoline described in the report rendered the test too severe for the particular purpose in view as suggested by Mr. Wolf; probably, indeed, the conditions of exposure were not sufficiently drastic to bring out the full protective effect which had been induced. Although very little excess lanoline remained, the heat-treatment would undoubtedly result in its penetrating into the metal to some extent; in addition a certain amount of chemical change would probably take place at the surface, resulting in a still more resistant layer. The treatment happened to be, in fact, very similar to that devised by J. J. Manley,<sup>15</sup> for the protection of brass weights, except that Manley used linseed oil, combined with much more drastic heating. The author believed that more favourable figures would have been obtained in the present tests if the excess of lanoline had been removed more completely. This did not affect Mr. Wolff's remarks concerning complete immersion conditions.

The author fully agreed with Professor Merrett as to the importance of "metal-colouring" in connection with atmospheric corrosion. He thought, however, that the work had demonstrated the great difference in the protection afforded by oxide and sulphide films respectively, notwithstanding that the initial appearance might be very similar. The results suggested that in selecting from the innumerable products of the metal-colourer's art, preference should be given, from the point of view of protection, to those films having an oxide, as distinct from a sulphide base. The permanence of the Japanese specimens described by Professor Merrett seemed to afford a good illustration of that principle; it was interesting to note that in those cases the film of oxide was obtained by the decomposition of water.

In reply to Mr. Field and Mr. Patterson concerning the comparative absence of seasonal fluctuations in the surrosion curve for zinc, he stated that, under unsaturated conditions of humidity, wide variations in the atmospheric sulphur content had relatively little effect on the surrosion of freshly cleaned metal; this was brought out by reference to Fig. 8, where curves A and D represented periods of maximum and minimum sulphur content respectively (*cf.* Fig. 1). This did not mean, however, that some such mechanism as that suggested did not assist in maintaining the linear relationship; the suggestion was worthy of serious consideration. The author was glad to have confirmation from Messrs. Field and Patterson as to the idea of "critical humidity"; his colleague, Mr. J. C. Hudson, had obtained a number of results bearing upon the greatly increased rate of attack upon zinc in the neighbourhood of the dew-point.

Dr. Vernon said he had already referred to Dr. Callendar's communication, and while he would look forward with interest to the forthcoming paper in which Dr. Callendar's results would be recorded more fully, he was glad that some account of such important work had been included in the present discussion.

Of the two explanations which Professor Benedicks had put forward as to the reason for the agreement in weight-increment of zinc specimens having very different surface conditions, the author preferred the second; the conception of "point-surrosion" was a helpful one and appeared to throw light on the initial disposition of the weight-increment/time curve.

<sup>14</sup> See also, J. S. Dunn, *Proc. Roy. Soc.*, 1926 (A), **III**, 210.

<sup>15</sup> *Phil. Mag.*, 1922, **44**, 948.

He could not see, however, that the evidence favoured the view that the action in the case of zinc was electrolytic in character. He admitted that his own work upon zinc was very incomplete, so much time having been taken up in connection with the tarnishing of copper, so that the initial mechanism of zinc surrosion was still obscure to him. He noted with interest Professor Benedicks' confirmation of the curiously unfavourable behaviour of very pure copper towards atmospheric corrosion, which he (Professor Benedicks) connected with the cuprous oxide content of the copper. The high resistance displayed by other grades of copper must clearly be attributed to the development of resistant films through the presence of specific elements in the metal, but hitherto he had regarded the H.C. copper as having suffered merely by comparison. Professor Benedicks' explanation as to the effect of cuprous oxide had not occurred to him. He was impressed by the fact that Professor Benedicks' conclusion was also reached by Mr. Smout.

The specific information Mr. Smout had given concerning the influence of cuprous oxide and of arsenic, together with other cognate matters, was valuable. He regretted he could not give the detailed analyses for which Mr. Smout had asked. The copper and zinc employed in "Series A" (p. 166) were of high conductivity and high-grade re-distilled quality respectively (the brasses were also of special purity); an analysis of the zinc appeared on p. 933 of the First Report. In the case of copper he suggested that the vital effects of small amounts of added elements having been definitely established, the further question of very small traces might well be made the subject of investigation.

Dr. Friend's communication pointed to some of the difficulties peculiar to corrosion research. The publication of the results of Dr. Friend's extensive series of field tests would be anticipated with interest.

Professor Bannister has raised a point of great interest in connection with the relative behaviour of iron and the non-ferrous metals after the lapse of many centuries. Considering, for example, iron and copper, the corrosion curves of which were represented by parabolas about the vertical and horizontal axes respectively (*cf.* Fig. 23B and Fig. 12 of the First Report) and bearing in mind the friable and compact nature of the respective corrosion products, it was not difficult to realise that copper specimens would remain intact after similar specimens of iron had long since disappeared. Later work had shown the important part played by hygroscopic solid particles in the atmospheric rusting of iron, leading to marked acceleration in the rate of attack even under conditions well below the dew-point. It was interesting, therefore, to note that the atmosphere of Egypt, highly charged with hygroscopic particles as it was, would provide ideal conditions for that type of attack, from which copper and bronze were relatively immune; it was significant also, as Professor Bannister had pointed out, that the ancient iron specimens which had survived had been protected largely from atmospheric dust as well as from moisture.

In conclusion Dr. Vernon again expressed his appreciation of the assistance he had received during the prosecution of the work, and of the action of the Research Association in permitting the publication of the Report.

**The President** in thanking Dr. Vernon for reading the paper, and the speakers for their contributions, expressed as had all the speakers, his appreciation of the sustained accuracy which characterised the work and of the patience and skill with which it had been carried through.

# THE PROBLEM OF THE SURFACE TENSION OF MERCURY AND THE ACTION OF AQUEOUS SOLUTIONS ON A MERCURY SURFACE.\*

BY R. S. BURDON AND M. L. OLIPHANT.

(Received January 11th, 1927.)

The following is a brief survey of the present position of the knowledge concerning the value of the surface tension of mercury, together with an account of further experiments on the spreading of aqueous solutions of acid upon a mercury surface and observations of the effect of different gases on the spreading of water and of dilute acids.

Apparent contradictions of the theory of Hardy and Harkins as to the spreading coefficient are also pointed out and it is shown how Antonow's rule can be reconciled with the observed phenomena.

## The Surface Tension of Mercury.

This has received more attention than that of any other substance except possibly water. The wealth of papers on the subject is equalled by the remarkable lack of uniformity in the values obtained. The subject is of interest at the present juncture because of the suggestion of certain workers,<sup>1, 2</sup> that the behaviour of a mercury surface will eventually be explained in terms of orientation of the atoms. Many writers have remarked on the extreme difficulty of obtaining and keeping a "clean" mercury surface, but it is probable that in the past too much of the diversity in the values obtained for the surface tension of mercury has been attributed to contamination and faulty manipulation. This is emphasised by the fact that more recent workers, taking the most elaborate precautions, do not obtain results in agreement with each other.

In considering the great number of papers on this subject, two determinations that must receive serious consideration are those of Harkins,<sup>3</sup> by the method of drop weight; and of Popesco,<sup>1</sup> by the method of the large drop. The latter method depends only on the difference in height of the top and the equator of a large circular drop of mercury resting on a flat plate or in a circular depression. In such a case the form of the upper part of the drop (which alone is used in measurement) must be independent of angle of contact with the lower plate. The drop-weight method is also claimed to be independent of contact angle, and both are classed as "static" methods.<sup>4</sup> For mercury against its own vapour, Harkins obtains a value

\* A contribution to the General Discussion on Phenomena at Interfaces.—See Vol. XXII., p. 433.

<sup>1</sup> Popesco, *Ann. de Phys.*, 1925, 3, 402.

<sup>2</sup> Perucca, *Comptes Rendus*, 1922, 175, 519.

<sup>3</sup> Harkins, *J. Am. Chem. Soc.*, 1920.

<sup>4</sup> Rideal, *Intro. to Surface Chemistry*, 4.

474 dynes per cm. while Popesco's value is 436.3 dynes. In dry air, Harkins obtained values lying between 459 and 464 while Popesco's value for a drop formed in dry air is 517 five seconds after formation, the value falling rapidly at first and then, more slowly, to approximately 440 after one hour. If the drop was formed in vacuo, however, the subsequent admission of air caused no rise in surface tension. For drops formed in air at less than atmospheric pressure, the initial surface tension appears to vary approximately linearly with the pressure of the air.

Popesco's explanation is essentially that 436 dynes/cm. is the value for a mercury surface in which the atoms have become oriented and have reached a fairly stable state. The presence of gas, however, tends to prevent orientation by the impact of gas molecules on the surface and hence gives larger values for the surface tension. In a gas the orientation of the surface atoms goes on progressively and most rapidly in hydrogen. The values obtained by Popesco 5 and 10 seconds after formation in  $H_2$ ,  $O_2$ , and  $N_2$  are:

Gas.	After 5 secs.	After 10 secs.
$H_2$	510	477
$O_2$	525	505
$N_2$	540	524

Meyer in 1898, using the method of ripples, obtained values that can be reconciled with Popesco's measurements but not with his conclusions. Meyer's values would be for a surface only a small fraction of a second after its formation and, hence, if the only effect of the gas is to impede orientation Meyer's values should be higher for all gases. His values actually are higher for  $H_2$ (554) but lower for  $O_2$ (505) and  $N_2$ (504). Now, though it is most improbable that an adsorbed layer should have the effect of raising surface tension, yet a comparison of Meyer's and Popesco's figures indicates that possibly a mercury surface, on exposure to a gas grows rapidly in surface tension (reaching a maximum much sooner in  $H_2$  than in other gases) and then falls. In any case it becomes of great interest to know what happens to the surface tension of a mercury surface during the first five seconds after its formation. After checking, by means of the apparatus described later (p. 210) that Popesco's values could be reproduced to a close approximation, the authors endeavoured to follow the behaviour of mercury under various times of exposure to dry air (or other gases), by means of the drop-weight method. An apparatus was manufactured to enable mercury drops to be formed from the same tip either in gases or in vacuo at any desired rate. Independently of theory as to the connection between drop weight and absolute value of the surface tension, it may be assumed that drops of the same liquid formed at equal rates from the same tip should have weights whose differences are very nearly proportional to the differences in surface tension.<sup>5</sup> Hence by taking weights for drops formed at, say, one per second in dry air and then in vacuo, it was expected to detect the effect of one second's exposure to air. By varying the drop rate the effects of different times of exposure would be found.

*Results and Discussion.*—The weights for ten drops were found to be very consistent, but for all rates of formation from three drops per second to one drop in 30 seconds the weight of a drop formed in air exceeded the weight of a drop formed in vacuo at the same rate by only approximately

<sup>5</sup> Not exactly, since the surface tension changes without change of density and hence drops formed at the same rate are not exactly similar in form. (Rideal, p. 14.)

one per cent. It was of course known that previous workers, Harkins,<sup>5</sup> Hogness<sup>6</sup> and Cenac<sup>7</sup> had found very small differences between the drop weight of mercury in air and vacuo, but it seemed possible that the long time taken in forming the drop might be a cause of this, since the surface tension falls rapidly with exposure to air. The present work shows that the drop-weight method fails entirely to show up differences in the value for air and vacuum, though these differences are shown up by the fact that a "large drop" of mercury is always deeper when formed in air than in vacuo. The negative result may mean that there is something wrong with the drop-weight method as applied to mercury, or that the effect of air on the surface is really not present in the drop-weight method. The latter alternative is not impossible since the formation of a drop at the end of a tube involves the continual expansion of the surface, and even where the drop is formed very slowly the actual motion of breaking away is quite rapid. A number of observers have commented on the way in which an expanding mercury surface differs in properties from a stationary surface,<sup>8</sup> A drop of water which fails to spread when placed on a mercury surface is often caused to spread by the action of pouring the mercury out of the dish, this involving the creation of new surface. Regarding the absolute value of the surface tension of mercury in vacuo, it may be said that different observers using the large drop method agree very closely with 436 dynes/cm. Results from the method of maximum bubble pressure (in H<sub>2</sub>) agree generally with those of the drop-weight method, while measurement of ripples and waves on a jet tend to the value found by the big drop method.

Concerning the drop-weight method as applied to mercury two points call for comment. Firstly the method depends on the assumption that the capillary rise method gives the correct value for the surface tension of water, but the fact that careful workers<sup>9</sup> have obtained values which differ with the kind of glass used for the tube does not seem to have been disposed of by modern workers. Secondly, the method has been based on measurements of liquid drops of approximately unit density which hang from the outer circumference of the tube, and there does not seem to be much experimental evidence for the belief that drops will have the same form for liquids of high density that do not wet the tube. At present it may be said that the big drop method is the simplest for following changes of surface tension, but it is not possible to take a reading for some seconds after the drop is formed. A method of getting over this difficulty is still being sought. As to absolute values there does not appear to be any objection to the mathematical basis of the method, but it is unfortunate that it has been used very little except for molten metals (chiefly mercury). Measurements on less dense substances by this method would be valuable.

The drop-weight method for mercury must still be held suspect until an explanation is found for the approximate equality of drop weight in air and vacuo.

### Aqueous Solutions on the Surface of Mercury.

In a previous paper one of us<sup>10</sup> described some phenomena presented by solutions spreading over the surface of mercury in air. The following is a report of further work on this subject.

<sup>5</sup> *J. Am. Chem. Soc.*, **43** (1921), 1621.

<sup>7</sup> *Ann. Chim. et Phys.* (1913), 299.

<sup>6</sup> Schofield, *Phil. Mag.*, March, 1926.

<sup>9</sup> Volkmann, *Ann. Physik*, **66**, 1898.

<sup>10</sup> *Proc. physical Soc.*, **38**, Feb., 1926.

It was shown that pure water spreads very slowly, solutions of neutral inorganic salts and of acids rapidly, and solutions of inorganic bases not at all. Drops of very dilute solutions of inorganic acids spread rapidly to cover a definite area and then stopped, the area covered during the rapid stage being approximately 1 sq. cm. for each  $10^{14}$  atoms of monobasic acid present, the figures being, for  $\text{HNO}_3$   $0.90 \times 10^{14}$  atoms per sq. cm., for  $\text{HCl}$   $1.0 \times 10^{14}$ , and for  $\text{HBr}$   $1.2 \times 10^{14}$ , each molecule of acid covering approximately ten atoms of mercury. A number of acids both organic and inorganic have now been tested using '0001 normal solutions and, in general, the differences have been much less than those indicated above. In fact, for all the acids tested it may be said that a drop of '0001 normal solution placed on a clean mercury surface spreads rapidly to occupy an area very closely equal to 1 sq. cm. for each  $10^{14}\text{H}$  ions given by the complete neutralisation of the acid. The area covered per molecule for  $\text{H}_2\text{SO}_4$  and other dibasic acids is twice as great as for  $\text{HCl}$ , moreover the solutions of the organic acids, oxalic, succinic, and phthalic, spread as fast and cover as great an area as the sulphuric acid.

In order to test whether any progressive change in behaviour occurred with progressive change in the acid molecule, readings were taken with '0001 normal solutions of the five organic acids, formic, acetic, propionic, butyric, and valerianic, using drops from the same pipette and observing the area covered during the rapid stage of spreading. The following results were obtained:

Acid.	Number of Molecules per sq. cm. covered $\times 10^{14}$ .
Formic, $\text{H.COOH}$ . . . .	96
Acetic, $\text{H.CH}_3\text{COOH}$ . . . .	102
Propionic, $\text{H(CH}_2)_2\text{COOH}$ . . . .	98
Butyric, $\text{H(CH}_2)_3\text{COOH}$ . . . .	92
Valeric, $\text{H(CH}_2)_4\text{COOH}$ . . . .	97

The differences obtained are only of the same order as the possible experimental errors involved in the dilution and measurement of area.

Even at the dilutions used these acids differ by over 50 per cent in their degrees of ionisation, yet they appear identical in their behaviour on a mercury surface. A drop of any one of them within about one second spreads to a definite area and stops, the action being completed approximately as quickly for valeric acid as for hydrochloric. This may indicate either that the neutral molecule is concerned in the spreading, or that the mercury absorbs the ions available with extreme speed and fresh molecules then dissociate.

*Electrically Aided Spreading.*—The very general appearance of the number  $10^{14}$  ions per sq. cm. directed attention to one of the electrical phenomena recorded in the early paper, *viz.* that if the positive terminal of a battery be placed in the mercury and the other in the drop of solution, then spreading is caused if the mercury be positive, but retarded if the mercury be negative. (In the latter case a forced spreading occurs if the voltage be high enough, the drop immediately contracting when the circuit is broken.) It was decided to try the effect of forcing  $10^{14}$  electrons through a drop of distilled water on the surface of mercury. A platinum terminal was placed in the mercury and a liquid terminal<sup>10</sup> placed in a drop of water on the mercury surface. First of all the effect of discharging a condenser through the drop was tried, but the results were not very consistent, largely owing to the uncertainty as to when the condenser had

completely discharged. Next a battery, safety resistance and microammeter were placed in series in the circuit. A drop of distilled water was placed on the mercury, the terminals inserted and current switched on for ten seconds and then the area of the drop was measured. The difference between this area and that of a similar drop left on open circuit for the same time gave the extra area covered owing to the current. A current of 16 microamps. caused an increase in area of one sq. cm. per second for pure water on a clean mercury surface. But one electron =  $1.57 \times 10^{-19}$  coulombs and, therefore, a current of 16 microamps. in one second delivers:

$$16 \times 10^{-6} \div 1.57 \times 10^{-19} = 1.0 \times 10^{14} \text{ electrons.}$$

It may be, then, that absolutely pure water is perfectly neutral so far as its tendency to spread on mercury is concerned, but that it will spread to cover one sq. cm. for each  $10^{14}$  monovalent negative ions present, whether these are provided by an acid dissolved in the water or whether they are sorted out from the water itself by means of an electric current. If any factors are present to prevent spreading, *e.g.* bases in solution or contamination on the mercury surface, then the areas covered are much less. The rate of spreading without current is not affected by earthing the mercury or the solution or both.

### Mechanism of Spreading.

It is difficult to picture any mechanism accounting for spreading, since it is practically inconceivable that all the acid molecules in a drop of solution could reach the surface in the short time involved. It was first suggested by Mr. A. V. Slater<sup>10</sup> that the definite area covered was due to adsorption of ions with attendant water molecules, thus accounting for the large area covered. At first the fact that the drops spread to an appreciably larger area on warm mercury seemed to contradict this hypothesis, but it is quite possible that at the higher temperature the water itself supplies the extra ions. The increased spreading due to this would not depend on the number of extra ions present in the water at any instant, but on the rate at which these ions, when absorbed at the surface, are replaced by further dissociation of the water.

It seems necessary to postulate an action analogous to the "squeezing action" suggested by Edser to account for the spreading. The adsorbed ionic groups, with the mercury atoms to which they are attached, are free to move on the surface with only fluid friction and, hence, if the attraction of the underlying mercury surface extends beyond the primary adsorbed layer this latter will be jostled out, and spread will occur and continue so long as the supply of negative ions lasts.

Two observations support this view:

(1) So far as can be seen by eye the drop spreads more slowly at first, the rate of growth of diameter increasing with the area covered. Now if spreading is due to any action at the edge of the spreading drop then at most the diameter should increase uniformly, whereas if spreading is due to forces between the comparatively more distant parts of the drop exerting a "squeezing-out" action, then the linear rate of spreading should increase with the area over which this squeezing action can occur. It is proposed later to determine, if possible, the connection between instantaneous area and rate of spread by means of a cinema picture of the spreading drop.

(2) If when one drop has spread to a disc and stopped, a second drop of solution be placed on the middle of the disc, then the solution spreads to cover double the area in a time shorter than that taken by the spreading of the first drop. *Lycopodium* sprinkled on the first disc indicates that the spreading takes place from the centre as would be expected on the squeezing theory.

On this view adsorption takes place on a continually renewed surface, as the adsorbed ions move outwards carrying with them the mercury atoms to which they are attached. This seems in accord with the observation that water will spread on a mercury surface for which the spreading coefficient of Hardy and Harkins is negative. This point will be discussed later.

If there already exists on the surface an adsorbed film of liquid or solid, due to contamination, etc., spread will only occur so far as the spreading substance is able to compress this film. If the adsorbed film is gaseous the life of any gas molecule in the surface is exceedingly short at ordinary temperatures, and it is easily replaced by a more stable ion or molecule, so that even distilled water will spread slowly on a surface which has been in contact with a gas for 18 hours. The adsorbed layer of negative ions may be covered with a secondary layer of positive ions, so that the whole phenomenon is equivalent to an adsorption of the neutral molecule, as found by Schofield<sup>8</sup> and others.

Some light has been thrown on these problems by experiments made with the apparatus described below, by means of which it is possible to form surfaces of mercury under a variety of conditions, and to observe the behaviour of water or other liquids dropped upon them. Simultaneous measurements of the height of the big drop of mercury used are also possible, so that the changes in surface tension produced during spreading can be followed.

The vessel "A" is a large Pyrex beaker with the bottom removed and plate glass end-plates cemented on with red sealing wax. A large drop of mercury can be prepared on the slightly concave surface "S" by turning on

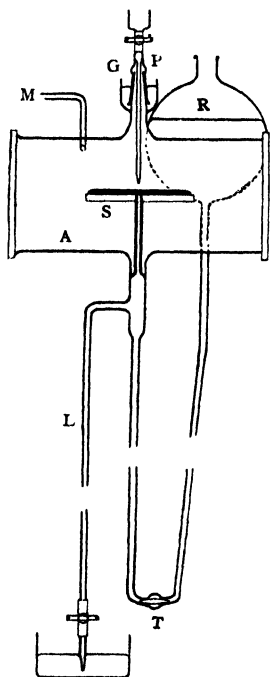


FIG. 1.

the tap "T" and allowing mercury to flow in from the reservoir "R". The tap "T" is about 80 cms. below the level of the side tube "L," so that although it is impossible to grease the tap, no air will leak in even when the apparatus is evacuated. The tube "M" is connected through a two-way tap and drying tubes to a vacuum pump, and also to a reservoir of gas provided with purifying and drying tubes. The ground glass join "G" is mercury sealed and can be closed by a ground cone of glass, or provided with a pipette "P" as shown, so that drops of liquid can be allowed to fall upon the mercury surface without admitting any trace of air.

After any experiment the mercury is drained away from "S" through the side tube "L" and the glass plate repeatedly washed with clean mercury. The plate glass windows allow the height of the drop to be photographed

in the manner described by Popesco.<sup>1</sup> The whole apparatus is mounted on a levelling table so that the concave surface "S" can be set truly horizontal. Although thick-walled rubber tubing and a clip are used to admit liquids through the pipette (as it is not possible to grease a tap), it was found that by tightly screwing up this clip the apparatus could be evacuated to a "black vacuum" by means of a condensation pump, and a high degree of evacuation could be maintained for hours without running the pump. The mercury surface found in a dried and purified gas is remarkably free from contamination, and water spreads rapidly and uniformly right up to and even over the edge. The argon used in the experiments was purified by passage over heated metallic calcium. The oxygen was a carefully dried commercial product, but otherwise was used as it left the cylinder.

### Results.

*The Effect of Gases on Spreading.*—Water spreads rapidly on a surface prepared in pure dry air or argon, but spreads even more rapidly on a surface prepared in oxygen. Oxygen appears to play an important part in the spreading in many cases. For instance, when a solution of HCl which is not too dilute spreads and evaporates in air or oxygen, a white film of calomel is left behind on the surface. This film does not appear to contaminate the surface to any large extent, for a second drop of acid will spread, pushing the solid layer to one side. On the other hand, if the drop is formed in argon that is free from oxygen and the HCl is placed on the surface, it spreads as before, and evaporates, but no visible deposit is formed, though the behaviour of a second drop of acid shows that the surface is badly contaminated. The effects of oxygen are most marked when the mercury surface is prepared in vacuo and the gas then admitted.

*The Spreading Coefficient and Antonow's Rule.*—It appears at first that neither of these rules is applicable in general to mercury-water, or to mercury-acid solution interfaces. For instance water spreads well on a surface of mercury freshly formed in a gas such as air or argon and, if we accept the values for the surface tension of mercury given by the large drop method, *viz.* 500 dynes/cm. for a fresh surface in air, 427 for the interfacial tension water-mercury, the spreading coefficient of Hardy and Harkins has a positive value :

$$\sigma_{\text{Hg}} > \sigma_{\text{Hg} - \text{H}_2\text{O}} + \sigma_{\text{H}_2\text{O}}$$

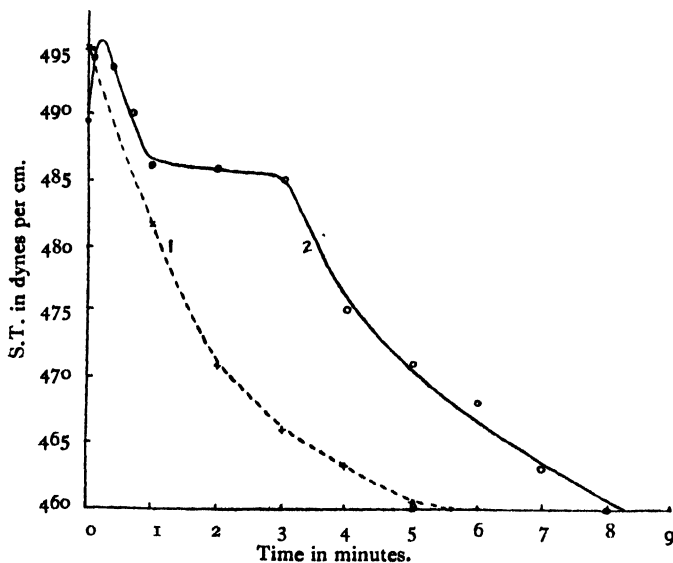
However, for a drop prepared in vacuo, gas being subsequently admitted ( $\sigma = 436$ ), the spreading coefficient must have a negative value of about 60. Spread always occurs, though very much more sluggishly than in the first case. If the gas admitted be argon the surface tension possesses the same initial value of 436 dynes/cm., but spread does not now occur although the drops of water flatten slightly. If oxygen be admitted spread occurs quite rapidly, so that it appears that here again oxygen is a controlling factor. Water also shows a positive tendency to spread in vacuo on a drop formed in vacuo.

When water spreads on a surface prepared in vacuo, or on mercury which has been exposed to air for some time, the spreading coefficient is negative, and the water must be spreading against a pressure of some 60 dynes/cm. if the interfacial tension possesses its normal value, and the adsorbed film of water molecules is hence subjected to a lateral compression of this amount. As has already been pointed out, it is probable that spread

occurs always on a freshly renewed surface, so that it would seem permissible to assume the normal value of the interfacial tension. In several experiments on spreading in such cases a rise in the height of the large drop, indicating an increase of surface tension, has been noted. This rise is very small, of the order of 4 or 5 dynes only, but it is consistently observed for older drops. It is difficult to form a satisfactory idea of the processes causing this increase in surface tension of the mercury.

Mr. R. Mitton working in this laboratory, has measured, by means of a sensitive torsion balance, the pressure exerted by spreading drops of acid on mercury, and finds for the spreading coefficient a value of 30 or 40 dynes, which is in general agreement with the above conclusions.

In the various experiments in which water has been observed to spread on mercury the surface tension of the latter has varied between about 500



(1) Graph of fall of S.T. of a large drop of Hg in dry air.

(2) Graph of fall of S.T. of a large drop of Hg with a droplet of water spreading on its surface.

FIG. 2.

dynes/cm. for a freshly prepared surface in argon or air, to about 400 for a surface which has stood in contact with a gas for some hours. Antonow's rule states that for a liquid which spreads on mercury the interfacial tension between it and mercury is equal to the difference between their individual surface tensions. The interfacial tension would then have to vary between 427 and 327 dynes/cm., which is improbable, but if we conclude that spread always occurs on a continually renewed surface the difficulty disappears to a large extent, for the S.T. of a freshly formed surface is greater than 500 dynes/cm., and the interfacial tension possesses its normal value.

### Conclusion.

The present paper is written as a contribution to a general discussion on surface phenomena. It draws attention to outstanding difficulties with regard to the surface tension of mercury; it may be said to be impro-

bable that agreement as to the absolute value of this quantity will ever be reached by mere repetition of measurements. The outstanding need at present is for a theoretical basis to account at least qualitatively for the differences between accurate determinations made by different methods.

The account given of further work on the spreading of aqueous solutions on mercury suggests, on the one hand, the existence of forces exerted over greater than molecular distances, and on the other hand, further supports the view that the ion is the determining factor in the spreading of these liquids.

In conclusion it is desired to express our thanks to Mr. H. Finlayson for advice and for assistance in obtaining pure samples of the acids used, and to Mr. F. J. Wauchope for much assistance in connection with both apparatus and observations.

*The University of Adelaide.*

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## THE ELECTRO-DEPOSITION OF IRON-NICKEL ALLOYS. PART I.

By S. GLASSTONE and T. E. SYMES.

(Received February 1st, 1927.)

The problem of the relationship between the proportion of nickel to iron in an electrolyte and the composition of the alloy which may be deposited by electrolysis from this solution is one of considerable practical and theoretical interest.<sup>1, 2</sup> Toepffer<sup>3</sup> worked with nickel and ferrous sulphate solutions to which ammonium sulphate or oxalate was added in some cases and found that the proportion of iron in the deposit decreased as the C.D. was increased from 0.7 to 7 amps./dm.<sup>2</sup> By extrapolating his results to zero C.D. Toepffer came to the improbable conclusion that the initial deposit consisted of pure iron. Küster<sup>4</sup> extended the observations to lower C.D.'s—down to 0.085 amp./dm.<sup>2</sup>—and concluded that with increasing current the proportion of iron in the deposit increases rapidly to a maximum value and then decreases slightly. This author states that the first few tenths of a milligram of deposit contains no iron, but this seems unlikely since nickel and iron form solid solutions. Engemann<sup>5</sup> in the course of some work on the peeling of electro-deposits of nickel, investigated the simultaneous deposition of iron and nickel from sulphate solutions. The general conclusions drawn from Engemann's results are (a) the deposit contains relatively more iron than the electrolyte, (b) the proportion of iron in the deposit increases to a maximum and then decreases as the C.D. is increased, (c) an increase in the acidity of the electrolyte results in a decrease in the proportion of iron in the deposit, and (d) the ratio of iron to nickel in the deposit decreases with increasing time of deposition. Kremann, Suchy and Maas<sup>6</sup> and Glasstone<sup>7</sup> worked at a uniform C.D. and found that the deposit from mixed sulphate solutions contained relatively more iron than did the electrolyte. In continuing the work of Brunı and

<sup>1</sup> Thompson, *Trans. Am. Electrochem. Soc.*, 1923, 44, 359.

<sup>2</sup> Glasstone, *J. Chem. Soc.*, 1926, 129, 2887, 2897.

<sup>3</sup> Diss. Breslau, 1899; see *Z. Electrochem.*, 1899, 6, 342.

<sup>4</sup> *Ibid.*, 1901, 7, 688.

<sup>5</sup> *Ibid.*, 1911, 17, 910.

<sup>6</sup> *Monatsh.*, 1913, 34, 1757.

<sup>7</sup> *Trans. Faraday Soc.*, 1924, 19, 574.

Amadori,<sup>8</sup> Benvenuti<sup>9</sup> worked at a C.D. of 0.05 amp./dm.<sup>2</sup> and observed that for an ammonium tartrate bath of nickel and iron the deposit contained relatively more or less iron than the electrolyte according as the latter contained less or more, respectively, than 74 per cent. of the total metal as iron.

In reviewing the previous work on the subject of the electro-deposition of alloys of iron and nickel (see also <sup>1</sup>), it is clear that only a very comprehensive investigation could throw light on the various factors affecting the composition of the deposit; this work has been undertaken and the present report deals with the influence of (i) hydrogen-ion concentration, (ii) current-density, (iii) time, and (iv) rotation of the electrode, on the composition of iron-nickel alloys deposited from various mixed solutions of nickel and ferrous sulphates at a temperature of roughly 15°.

In no previous investigation of this type had the attempt been made to fix definitely the hydrogen-ion concentration of the solution by means of buffer mixtures. If this factor is of any importance at all, and it must at least influence the current efficiency for metal deposition, then buffering is essential because otherwise the hydrogen-ion concentration in the vicinity of the cathode is certain to be considerably less than in the bulk of the electrolyte. In the electro-deposition of metals from solutions containing ferrous iron, it is necessary to separate anode and cathode compartments in order to avoid oxidation of the electrolyte, since ferric ions cause the deposited metal to become black and coarse instead of smooth and shiny; consequently the acidity of the cathode solution will decrease steadily throughout the run of an experiment. By the use of a buffer mixture this rate of decrease is greatly diminished and, by adding acid to the cathode liquid at definite intervals, the hydrogen-ion concentration may be kept within very narrow limits.

In the present work all the electrolytic solutions were buffered by the use of sodium acetate-acetic acid mixtures<sup>10</sup> of a total concentration of 0.5 g.-equiv. per litre; by adding acetic acid from time to time the hydrogen-ion concentration of the solution never altered by more than 0.2 units of  $p_H$ . By means of these buffer mixtures the effect of varying the hydrogen-ion concentration of the solution one-hundred fold (from  $p_H$  3.2 to 5.2) was investigated; this range is ten times that used by Engemann,<sup>5</sup> in whose experiments, however, the hydrogen-ion concentration in the vicinity of the cathode may not have been at all constant. A complete investigation of the variation in the composition of the deposited alloy from electrolytes containing varying ratios of iron and nickel at  $p_H$  values of 3.2, 4.0 and 5.2 has been made at a series of C.D.'s varying roughly from 0.01 to 5 amps./dm.<sup>2</sup>; the results of this work are described below.

No information is yet available as to the effect of the anions present in the solution on the composition of the alloy, but this factor, as well as others, will be investigated later.

### Experimental.

*Preparation of Electrolyte.*—The basis of every electrolyte used in the present work was a sodium acetate-acetic acid buffer solution of a total concentration of 0.5 g.-equiv. per litre; the salt and acid were used in the

<sup>8</sup> *Atti Accad. Sci. Padova*, 1914, 30, 349.

<sup>9</sup> *Atti R. Inst. Veneto Sci.*, 1916, 76, 453.

<sup>10</sup> Walpole, *J. Chem. Soc.*, 1914, 105, 2501.

proportion<sup>10</sup> of 0.6 to 19.4 equiv. for a solution of  $p_H$  3.2; 3.6 to 16.4 for  $p_H$  4.0 and 15.8 to 4.2 for  $p_H$  5.2. Weighed quantities of nickel and ferrous sulphates in appropriate amounts were then added to the buffer mixtures and the resulting solutions were used in the cathode compartments of the electrolytic baths. The total concentration of iron and nickel was always either 2 or 0.4 g. equiv. per litre. The nickel sulphate and sodium acetate were the "Recryst." variety supplied by the British Drug Houses, whilst the ferrous sulphate was of A.R. standard. The nickel salt was found to contain traces of cobalt.

*Cathodes.*—The cathodes were of thin sheet copper and were of different sizes varying from 2 sq. cm. to 25 sq. cm. in exposed area; the larger ones were used for experiments at low C.D.'s and the smaller ones for high C.D.'s. It was found in early experiments that the treatment of the electrode, previous to its use as a cathode, affected the physical condition of the deposited alloy, although it appeared to have very little influence on the composition. The method generally adopted was to clean the surface of the copper by dipping the electrode into strong nitric acid and then washing immediately with a stream of water. The electrode was then dried between filter paper and finally washed with a little ether, which was removed by warming over a flame. This preliminary treatment was found to give smooth adherent deposits which did not crack too easily. It was found, too, as the result of experiments, that the shape of the electrode had no appreciable influence on the composition of the deposited alloy and, in the present work, electrodes of a slightly oblong shape were found to be the most convenient.

*Anodes.*—The anodes were made of hard carbon such as is used in Leclanché cells. Pieces 2.5 cm. by 4.0 cm. and 0.8 cm. thick were soaked in molten paraffin wax for some time; they were then removed, allowed to cool and one face only, which was to act as the conducting face of the electrode, was scraped clean. Electrical contact was made by means of copper wire which passed through a hole near the top of the electrode and was wound tightly round the carbon.

*Arrangement of Apparatus.*—The electrolytic bath consisted of a vessel of 750 c.c. capacity in which was placed a porous earthenware pot capable of holding 200 c.c. The latter acted as the cathode compartment and was filled with the buffer solution containing nickel and ferrous sulphates, prepared as described above. The outer, or anode compartment was filled with the buffer solution only and contained no nickel or iron salt; the object of this was chiefly to obviate the danger of ferric salt passing into the cathode compartment. During the course of an experiment very little diffusion occurred and the concentration of the cathode compartment solution was not appreciably altered. The carbon anodes were placed symmetrically on either side of the outer compartment with the exposed faces directed inwards; the cathode, with both faces exposed, was placed midway between the anodes so that the three electrodes were parallel to one another.

*Experimental Method.*—The apparatus as described was set up; a weighed cathode was placed in the circuit and the current of known strength—measured by an ammeter—was switched on and the time noted. At intervals during the passage of the current a small quantity of the cathode liquid was removed, diluted if necessary with a small volume of distilled water, and a few drops of "bromphenol blue" or "methyl red" indicator, according to the  $p_H$  of the solution, added to a portion. The colour of the solution by transmitted light was then compared in the usual way

with that obtained by superimposing two tubes containing a colourless buffer solution of known hydrogen-ion concentration and the standard amount of indicator, and the diluted cathode liquid respectively. By this means the  $p_H$  of the solution was determined approximately—the salt error of the indicator being neglected—and if the value obtained differed by more than 0.1 unit from the original value, then re-adjustment was made by adding a solution of acetic acid (1.0 to 1.6 *N*) containing ferrous and nickel sulphates at the same concentration as in the original cathode solution; an equal volume of the cathode solution was withdrawn when the acetic acid was added. As the result of preliminary observations the correct rate of adding the acid solution was found and thus the hydrogen-ion concentration of the cathode liquid was kept almost constant throughout the whole of an experiment. For example when working with a solution of  $p_H$  3.2 it was necessary to add 25 c.c. of a 1.6 *N*-acetic acid solution every fifteen minutes to 200 c.c. of cathode liquid when a current of 0.12 amps. was passing; with smaller currents proportionately less acid solution was required. At  $p_H$  4.0 only 10 c.c. of a *N*-acetic acid solution were added every thirty minutes when 0.12 amps. was passing, whilst at  $p_H$  5.2 adjustment was only necessary occasionally. The continued addition of fresh nickel and ferrous sulphate with the acetic acid also helped to maintain the original concentration of these metals in the cathode liquid. After an appreciable deposit of alloy, varying from 0.035 to 0.005 grams, was obtained on the cathode the latter was removed and the time noted. The electrode was well washed with water, dried with filter paper, washed with ether, dried by warming and then weighed; the area of the electrode covered with deposited alloy was also carefully measured. The deposit was then analysed as follows.

*Analytical Method.*—The alloy was dissolved off from the electrode by means of dilute sulphuric acid or by a mixture of the acid with hydrogen peroxide solution; the latter method was only adopted when the alloy contained a large proportion of nickel. If any copper had been dissolved it was removed by precipitation with hydrogen sulphide after destroying the peroxide by boiling. A small amount of sodium sulphite was then added to the solution to ensure the presence of all the iron in the ferrous state and the excess of sulphur dioxide was boiled off; the liquid was cooled in the presence of carbon dioxide and the iron titrated with permanganate solution. Rochelle salt was then added and the solution made slightly alkaline with ammonium hydroxide; the nickel was estimated in this liquid by the potassium cyanide method.<sup>11</sup> The composition of the alloy was calculated from the results obtained in this analysis. It should be mentioned that, although the analytical method was tested and found to be satisfactory, the sum of the separate amounts of iron and nickel found was generally somewhat lower than the total weight of alloy deposited; this may have been due to the presence of hydrogen or carbon—although the latter was not observed—in the alloy.

*General.*—At each C.D. generally four, and frequently many more, different deposits were made by allowing the current to pass for varying periods of time. Preliminary experiments had shown that as long as the hydrogen-ion concentration of the solution and the current were kept constant the composition of the alloy did not in general vary appreciably with the time of deposition<sup>12</sup> (see also p. 225). Exact agreement was by

<sup>11</sup> Treadwell, "Quantitative Analysis," 1924, p. 613.

<sup>12</sup> It is possible that the first thin film of alloy which covered the copper electrode may have been of somewhat different composition, but the analytical method was not exact enough for such small amounts to be determined with reasonable accuracy.

no means always obtained between the analyses of different specimens deposited apparently under identical conditions; this variation, of the order of one per cent., may have been due to differences in the electrode surface, local differences of  $p_H$  or of the composition of the solution due to diffusion, or other disturbing factors which could not be eliminated. Consequently all the results obtained with a given electrolyte were plotted on a graph and a smooth curve was drawn through the series of points.

The cathode solutions were completely renewed from time to time as signs of oxidation of the iron became apparent; since comparatively small amounts of metal were deposited the concentration of the solution was never appreciably altered. The following twenty solutions were used as electrolytes in the present work; the total concentration of iron and nickel is expressed in g.-equivs. per litre and the expression "per cent. of iron" (Fe %) refers to the ratio of the number of atoms of iron to total iron and nickel in the electrolyte:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
$p_H$	3.2	3.2	3.2	3.2	4.0	4.0	4.0	4.0	4.0	4.0
Fe+Ni	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0.4
Fe %	2	10	50	70	2	10	30	50	70	2
	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.
$p_H$	4.0	4.0	4.0	4.0	5.2	5.2	5.2	5.2	5.2	5.2
Fe+Ni	0.4	0.4	0.4	0.4	2.0	2.0	2.0	2.0	2.0	2.0
Fe %	10	30	50	70	2	10	30	50	70	90

The curves in Figs. 1, 2, 3, and 4 indicate the variation in the composition of the alloy deposited at different C.D.'s, in ampères per sq. dm., from the electrolytes described above. From the amount of alloy which was deposited in each experiment and the quantity of electricity which had passed through the cell the current efficiency was calculated in each case. Although the results obtained were not in very good agreement with one another yet certain definite tendencies were noticeable and, in order to show these, the mean efficiencies at a number of C.D.'s for solutions of  $p_H$  3.2, 4.0, and 5.2 are given in Table I.

TABLE I.

Per Cent. Current Efficiency for Alloy Deposition.				
C.D.	$p_H$ 3.2.	$p_H$ 4.0.	$p_H$ 4.0 (dil.).	$p_H$ 5.2.
0.1	1.6	4.8	3.2	48
0.25	2.4	7.2	8.0	56
0.5	4.8	16	16	64
1.0	16	29	24	80
2.0	19	38	35	80
4.0	26	43	40	80

In general the efficiencies were somewhat greater with the solutions containing a small proportion of iron, probably on account of the lower deposition potential of the alloy from these solutions.<sup>3</sup>

*Discussion of Results.*—An examination of Figs. 1, 2, 3 and 4, shows that with increasing C.D. the proportion of iron in the deposited alloy increases at first rapidly, then more slowly and finally reaches a maximum amount. After this maximum is reached further increase of C.D. has

almost no effect on the composition of the alloy in some cases, whereas in others, particularly when the solution contains only a small proportion of

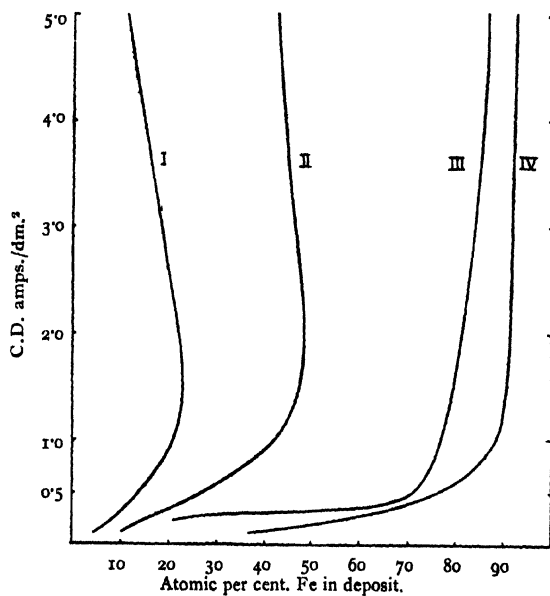


FIG. 1.

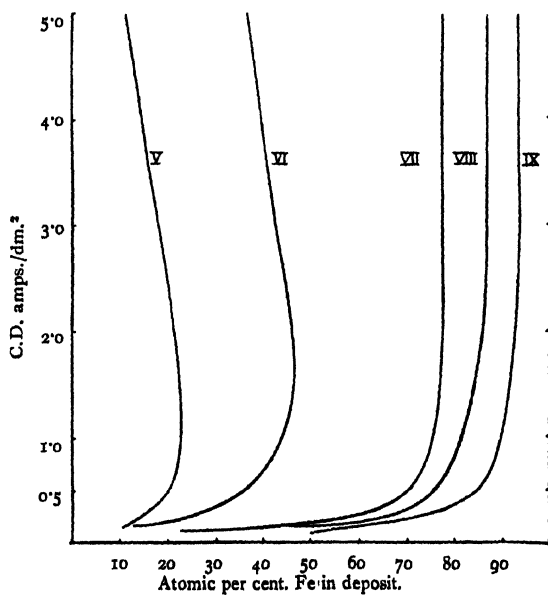


FIG. 2.

iron, the amount of iron in the deposit decreases quite considerably.<sup>2</sup> Owing to the rapid changes which occur in the alloy at low C.D.'s

it is clear that the composition of the initially deposited alloy at very low C.D.'s may be rather uncertain, but the results indicate definitely

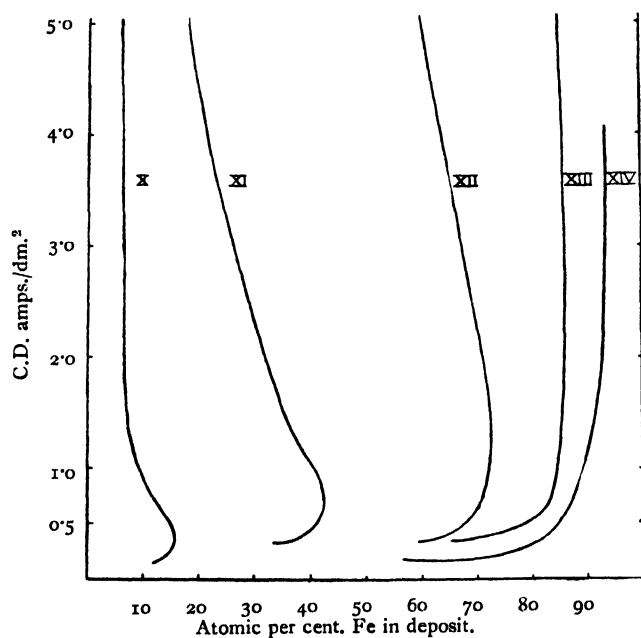


FIG. 3.

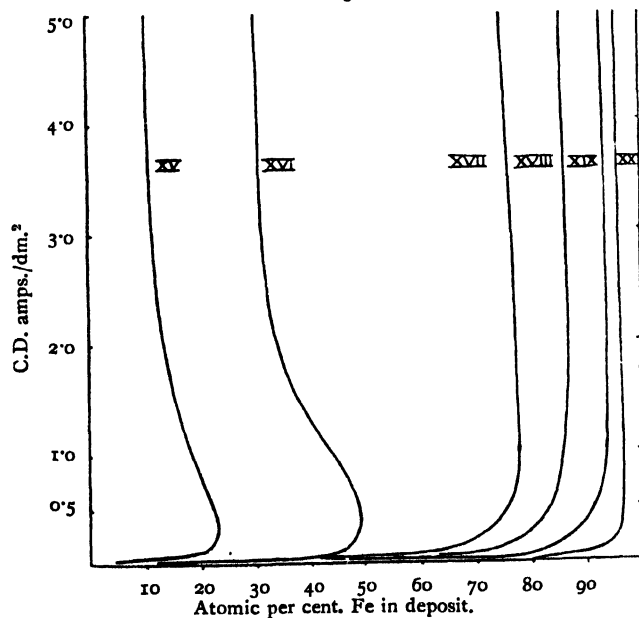


FIG. 4.

that for solutions containing 30 per cent., or more, of the total nickel and iron in solution as iron the initial deposit contains relatively less iron than

does the solution ;<sup>4</sup> this result is to be expected since nickel can deposit at a lower cathodic potential than iron. When the solution contains 2 per cent. and 10 per cent. of the total metal as iron, however, the initial deposit appears to contain a slightly greater proportion of iron than does the solution ; this may be due to a change in the composition of the deposit as the result of a small alteration in the C.D., but repeated observations with these solutions have never yielded an alloy containing relatively less iron than is present in the electrolyte. In the course of previous work one of us has put forward the suggestion that iron and nickel are deposited primarily in a metastable form which then changes spontaneously and at a definite rate into the normal form ; it was considered also that in the deposition of an alloy of these metals the presence of iron retards the change from metastable to stable nickel,<sup>2</sup> and so a more negative potential is required for the deposition of the latter. From an electrolyte containing a small proportion of iron the deposited alloy will in any case be poor in this metal and so the free energy of the iron will be less than in the pure state ; it will thus tend to be deposited at a lower cathodic potential. It is not unexpected, therefore, that a combination of this effect with the retarding effect of iron on the deposition of nickel results in the deposition at very low C.D.'s, from solutions containing relatively little iron, of alloys containing a larger proportion of iron to nickel than is present in the electrolyte. If the proportion of iron in the solution is increased, however, the deposited alloy will contain more iron and so the deposition potential of this metal, in the less dilute form, becomes more negative than that of nickel ; hence the initial deposits from solutions containing more than about 20 per cent. of the total metal as iron contain a relative excess of the more readily deposited metal, nickel.

As the C.D. is increased the cathodic potential is raised and hence the amount of iron in the deposit will increase ; it has already been suggested<sup>2</sup> that this increased proportion of iron will exert an increased retarding effect on the change of metastable to stable nickel with the result that the further deposition of this metal is inhibited. The deposit will thus tend to contain even less nickel, and so with increasing C.D. the proportion of iron should increase rapidly ; this has been actually found to be the case with every solution examined. The tendency for the amount of iron in the alloy to increase will be opposed by two factors ; firstly, since the alloy is becoming poorer in nickel the deposition potential of this metal will be lowered, and secondly, the solution in the vicinity of the electrode will become relatively richer in nickel ions since the deposit contains relatively more iron. These two factors will tend to make the alloy richer in nickel and hence, as the C.D. is increased, a point of balance is reached at which the opposing factors neutralise one another and the composition of the alloy remains constant even if the C.D. is further increased. If the electrolyte is fairly concentrated in iron and nickel salts, for example two g.-equiv. per litre, diffusion will in general keep pace with the deposition of metal and the balance reached in the composition of the alloy will be due mainly to the decrease in the free energy of the nickel. In this case the composition of the alloy will remain independent of the C.D. until such time as the rate of deposition is very great and exceeds the rate of diffusion of fresh electrolyte up to the cathode ; this is actually found to be the case with solutions VII., VIII., IX., XVII., XVIII., XIX. and XX. If the original solution contains a small proportion of iron, say 2 per cent., then it can be readily shown that owing to the deposition of an alloy containing about 20 per

cent. of iron the solution in the vicinity of the cathode will become poor in ferrous ions quite soon and so after reaching a maximum the proportion of iron in the deposit must subsequently decrease with increasing C.D.; this occurs with solutions I, V, X, XI, XV. and XVI. With the more dilute solutions (0.4 g.-equiv. per litre) the effect of diffusion is more evident and is to be observed even with solutions containing 30 to 50 per cent. of the total metal as iron; this is not only shown by the shapes of the curves in Fig. 3, but also by a comparison of the compositions of the alloys deposited when the balance (or maximum) point is reached from solutions of differing total metal concentration but containing nickel and iron in the same proportion. This comparison may be made from the results given in Table II. With the solution containing 70 per cent.

TABLE II.

Total Concentration of Electrolyte	Maximum Per Cent. Iron in Deposit from Solutions Containing:				
	2 Per Cent. Fe.	10 Per Cent. Fe.	30 Per Cent. Fe.	50 Per Cent. Fe.	70 Per Cent. Fe.
2 g.-equiv./litre	22.4	46.5	77.4	87.1	93.5
0.4 " "	15.7	42.3	72.2	86.2	93.4

of the total metal as iron diffusion clearly plays no part in the attainment of the balance point; this is to be expected, since even if the deposit does contain relatively more iron than the solution the actual change in the composition of the electrolyte with such a large proportion of iron can be shown to be so small as not to affect appreciably the composition of the deposited alloy. In the case of the 50 per cent. iron solution the maximum percentage of iron attained in the dilute electrolyte is not quite as great as that reached in the concentrated solution; this shows that diffusion is beginning to exert a small influence. In the solutions containing a smaller proportion of iron it is clear from the results in Table II. that the rate of diffusion of the electrolyte up to the electrode is having some influence on the production of the point of balance; the composition of the alloys deposited at appreciable C.D.'s will thus depend not only on the ratio of iron to nickel in the electrolyte but also on the total concentration of the solution.

Another factor which may influence the composition of the solution in the vicinity of the cathode when working with an electrolyte of definite iron-nickel ratio is the rate of deposition at a given C.D. In a solution of  $p_H$  5.2, for example, the current efficiency for metal deposition is, of course, much greater than in a solution of  $p_H$  4 (see Table I.), and hence the effect of diffusion should be much more noticeable in the former solution than in a solution of equivalent iron and nickel concentration at  $p_H$  4; this is seen actually to be the case by comparing the results for solutions V., VI. and VII. ( $p_H$  4.0) with those for solutions XV., XVI. and XVII. ( $p_H$  5.2) respectively. The curves in Figs. 2 and 4 show that the decrease in the proportion of iron in the deposit with increasing C.D. is much more evident at  $p_H$  5.2 than at  $p_H$  4.0; the effect of diffusion is very pronounced with the 2 per cent. and 10 per cent. solutions at  $p_H$  5.2 (XV. and XVI.), and the curves resemble those obtained with a solution of  $p_H$  4.0 in which the total metal concentration is only 0.4

g.-equiv. per litre (Fig. 3, X. and XI.). In solutions of  $p_H$  3.2 the current efficiency is even less than when the  $p_H$  is 4, and hence the effect of diffusion will be less in the former case than in the latter; this is shown to be so by comparing the results for solutions I. and II. ( $p_H$  3.2) with those for solutions V. and VI. ( $p_H$  4.0).

*Effect of Stirring.*—In order to obtain further information concerning the part played by diffusion of the electrolyte in determining the composition of the iron-nickel alloy some experiments were carried out in which the cathode was rotated at a speed of approximately 550 revs. per minute; the experimental arrangement otherwise was exactly the same as before. Solutions VI., VII., XI., and XII. were used in this work and the average results for the compositions of the alloys deposited at various C.D.'s have been plotted

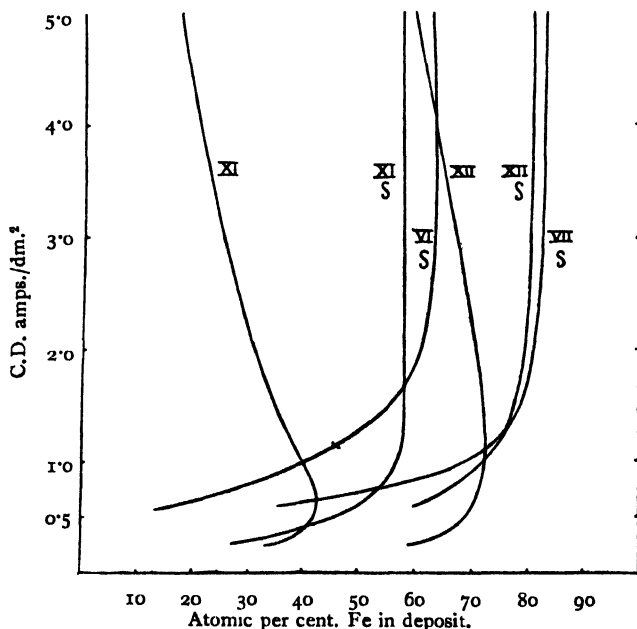


FIG. 5.

in Fig. 5 (curves marked with letter "s") together with those obtained from solutions XI. and XII. without stirring for purposes of comparison.

An examination of these curves shows that the change in the composition of the electro-deposited alloy caused by stirring the electrolyte is very striking; the results indicate clearly that the cause of the decrease in the proportion of iron in the deposit after the maximum or balance point is reached is the impoverishment of the iron content of the electrolyte near the cathode owing to the slowness of the diffusion process. If fresh electrolyte is brought up rapidly to the electrode then after the deposited alloy has reached its maximum iron content the composition remains unchanged although the C.D. may be increased. It should be mentioned that even in these cases in which the solutions were stirred the tendency for the proportion of iron in the deposit to decrease again was observed at very high C.D., namely in the vicinity of 11 amps./dm.² With the stirred solutions the alloys obtained at the balance point contained relatively more

iron than did those deposited from similar solutions which were not stirred ; the results are brought together for purposes of comparison in Table III.

TABLE III.

PERCENTAGE OF IRON IN DEPOSITED ALLOY.

					VI.	XI.	VII.	XII.
Solution unstirred	.	.	.	.	46.5	42.1	77.4	72.0
„ stirred	.	.	.	.	63.0	58.0	83.0	81.1

These results show that the composition of the alloy of maximum iron content obtained from the solutions under discussion very probably depends on the rate of diffusion of the electrolyte to the electrode.

The experiments with the rotating electrodes were also carried out with solution XIV. which has a total metal content of 0.4 g.-equiv. per litre, 70 per cent. of this being iron ; the C.D./composition of alloy curve obtained was almost identical, from 0.5 amps./dm.<sup>2</sup> upwards, with that given by the unstirred solution of the same composition and by the more concentrated solution (IX.) with the same iron-nickel ratio. The composition of the alloy containing the maximum amount of iron was also found to be independent of the concentration of the electrolyte or of stirring. This is exactly in accord with the views outlined above ; when the solution contains a large proportion of iron the electrolyte in the vicinity of the cathode always maintains a fairly constant iron-nickel ratio even if the main bulk of electrolyte is not very concentrated. In this case diffusion will not influence appreciably the composition of the alloy except at very high C.D.'s. It is probable, however, that diffusion effects would influence the composition of the deposited alloy even from electrolytes containing a large proportion of iron if the solutions were very dilute ; this change would not, in any case, be very great because under these conditions an alteration of the composition of the electrolyte causes only a small change in the composition of the deposited alloy (see, for example, curves XVIII., XIX., and XX. in Fig. 4).

*Influence of Hydrogen-Ion Concentration.*—If we examine the compositions of the alloys obtained at a given C.D. from solutions of different hydrogen-ion concentrations, it is difficult to detect any uniform tendency ; whilst at very low C.D.'s the deposits obtained from the more alkaline solutions appear to contain relatively more iron, those deposited at very high C.D.'s frequently contain less of this element. It has been repeatedly stated by one of us<sup>13</sup> that equal C.D.'s are not necessarily comparable when examining the behaviour of an electrode in different solutions ; in the present case, in order to determine the influence of the hydrogen-ion concentration of

TABLE IV.

Fe/Fe + Ni Per Cent in Solution.	Minimum Per Cent. Iron in Alloy.					Maximum Per Cent. Iron in Alloy.				
	2.	10.	30.	50.	70.	2.	10.	30.	50.	70.
$f_H$ 3.2	4.2	10.6	—	20.5	36.7	22.8	48.2	—	87.0?	93.0?
4.0	11.0	13.0	21.2	22.7	50.0	22.4	46.6	77.4	87.1	93.5
5.2	4.5	11.6	23.3	36.0	37.0	22.7	48.9	77.5	87.6	93.5

the electrolyte on the composition of the deposited alloy, it would be much more justifiable to compare the alloys obtained at equal cathodic potentials

<sup>13</sup> *J. Chem. Soc.*, 1924, 125, 2414 ; 1926, 129, 2887.

in different solutions, or possibly under such conditions that the alloys are being deposited at the same rate in the different cases. From previous work it is known that the cathodic potential for a given C.D. in general increases as the alkalinity of the solution increases and the results given in Table I. show that the rate of deposition of alloy also increases under the same conditions. A detailed comparison would, therefore, involve some difficulty, but a general comparison may be made by considering the initial deposits and those containing the maximum amount of iron obtained from solutions of various hydrogen-ion concentrations.

It has already been mentioned that the results at very low C.D.'s are only approximate; if this is taken into account it would appear that the hydrogen-ion concentration of the solution, within the limits of our experiments, has no influence on the composition of the initial deposit of iron-nickel alloy. This is in agreement with the observation<sup>2</sup> that the initial deposition potential of the alloy is also independent of the hydrogen-ion concentration of the solution.

Apart from diffusion the composition of the alloy obtained at the balance point, that is the alloy containing the maximum proportion of iron, should depend only on the relative tendencies of iron and nickel to deposit from solution. If we compare the compositions of the deposits obtained from solutions of equal total concentration of iron and nickel, we see that in general the maximum amount of iron in the deposit is also independent of the hydrogen-ion concentration of the solution. The results are least reliable in the solutions containing small proportions of iron because in these cases the effect of diffusion must be appreciable; if the solutions were stirred the maxima would be different, but still probably independent of the hydrogen-ion concentration. On the whole it may be concluded, therefore, that the hydrogen ion concentration does not directly influence the *relative* rates of deposition of iron and nickel from solutions containing simple salts of both metals. Any influence which hydrogen-ions may have is probably due to the fact that the current efficiencies are greater the smaller the concentration of hydrogen-ions; consequently the alloy is more easily deposited and the effect of diffusion enters at a lower C.D. in the more alkaline solutions.

### Discussion of Previous Work.

In his investigation on the composition of iron-nickel alloys deposited from solution Toepffer<sup>3</sup> used dilute electrolytes—total iron and nickel concentration 0.2 g.-equiv. per litre—and hence found that C.D.'s above 0.75 amp./dm.<sup>2</sup> the proportion of iron in the alloy decreased as the current was increased. It is clear, therefore, that Toepffer was working at C.D.'s above that at which the alloy of maximum iron content was deposited and the observed decrease in the iron content of the alloy, which was greatest with solutions containing a small proportion of iron, was due to the fact that diffusion of the electrolyte could not keep pace with the deposition of the alloy. This same argument applies to the limited observations of Foerster.<sup>14</sup> Küster<sup>4</sup> found that the alloys deposited at very low C.D.'s contained less iron than did the solutions, but that the proportion of iron increased rapidly with increasing C.D. (up to 0.67 amps./dm.<sup>2</sup>); these results are in agreement with those obtained in the present work. Engemann,<sup>5</sup> working chiefly at 50°, found that the alloy deposited at a C.D. of 1.25 amps./dm.<sup>2</sup> contained relatively more iron than did the solution and, for the electrolytes containing 2 per cent. and

<sup>14</sup> *Z. Elektrochem.*, 1897, 4, 160.

50 per cent. of the total metal as iron, the proportion of the latter in the alloy increased up to a maximum and then decreased again with increasing C.D. These observations are in agreement with those described in the present paper. Further, Engemann found that at a C.D. of 1.25 the proportion of iron in the deposit, obtained from a solution containing 2 per cent. iron, decreased with increasing acidity; this is to be expected since the more acid the solution the lower will be the rate of deposition of alloy and the closer will the composition approach that of the initial deposit with its low iron content. Quite different results, however, might have been obtained if the observations had been made at a very high C.D. when the effect of diffusion would have been important. The only conclusion of Engemann that is at all controversial is that the proportion of iron in the alloy decreases with increasing time of deposition. In the course of the present work deposits have been made for different times under a great variety of conditions, and it has been generally found, within the limits of the experimental errors of this work, that at C.D.'s below that at which the alloy of maximum iron content is deposited, or at the maximum point if diffusion is not influencing the results, the composition of the alloy does not vary with the time of deposition. The following example of results of experiments on solution VIII. at a C.D. of about 0.5 amp./dm.<sup>2</sup> is typical of many.

Time of Deposition. (Minutes.)	Weight of Deposit (Grams.)	Per Cent. Iron.
32	0.0044	78.1
32	0.0047	76.0
60	0.0080	76.3
60	0.0104	76.6
209	0.0295	76.0
209	0.0285	75.1
240	0.0324	76.2
240	0.0305	76.2

On the other hand if the experimental conditions are such that diffusion is influencing the composition of the alloy, then it has been frequently found, in agreement with Engemann's results, that the proportion of iron in the deposit decreases with increasing time. If Engemann's results are carefully examined, it is seen that the change in the composition of the alloy with time is greatest when the temperature is low, the C.D. high or when the solution only contains a small proportion of iron; these conditions are just those under which the effect of diffusion of the electrolyte will be greatest. It seems probable, therefore, that the changes in composition observed by Engemann, and under certain conditions in the present work, are due to changes in the concentration of the electrolyte in the immediate vicinity of the electrode. It is possible, too, that in Engemann's work changes in the hydrogen-ion concentration may have affected the rate of deposition and hence the composition of the alloy.

Kremann *et al.*,<sup>6</sup> and Glasstone,<sup>7</sup> worked at uniform C.D.'s of 1 and 4.5 amps./dm.<sup>2</sup> respectively and consequently it was found, in agreement with the present work, that the deposited alloy was always richer in iron than was the electrolyte from which it was deposited. The results obtained by Benvenuti<sup>9</sup> are probably fortuitous and depend merely on the arbitrary C.D. of 0.05 amp./dm.<sup>2</sup> at which the deposition of alloy was carried out; it is very likely that if another C.D. had been chosen entirely different

results would have been obtained. In any case it should be pointed out that in the ammonium tartrate bath used a large part of the iron, as well as much of the nickel, is present as complex ions, and hence the actual ratio of ferrous to nickel ions is very uncertain. The conclusions of Benvenuti as to the nature of the deposits are, therefore, of doubtful value.

*Physical Nature of Deposits.*—So far only very general observations have been made on the appearance of the alloys. In agreement with previous workers,<sup>1</sup> it has been found that iron-rich alloys are brighter than those rich in nickel, although the latter appear to be firmer and more adherent. The cleanliness and the previous treatment of the copper base used in the experiments affected the physical nature of the deposit; traces of grease caused the alloy to become scaly. Although thin deposits appear to adhere firmly to the cathode yet at high C.D.'s, after a thickness of about 0.01 mm. is reached, the deposits crack and can be removed quite cleanly from the copper electrode. At high C.D. also, particularly in dilute solutions, distinct "treeing" was observed at the edges of the deposit; this showed, in agreement with previous conclusions, that the ions were being discharged at the cathode faster than they were being replaced by diffusion.

### Summary.

(1) A complete investigation has been made of the compositions of the alloys deposited from well-buffered solutions of definite hydrogen-ion concentration containing various mixtures of ferrous and nickel sulphates at a series of C.D.'s ranging from 0.008 to 5.0 amps./dm.<sup>2</sup>.

(2) In every case the amount of iron in the deposit was found to increase rapidly with increasing C.D. and then more slowly until a maximum was reached; after this point further increase of the current caused the proportion of iron in the deposit either to remain constant or to decrease.

(3) The composition of the initially deposited alloy from any solution of given iron-nickel ratio appeared, like the deposition potential, to be independent of the hydrogen-ion concentration of the solution.

(4) From solutions containing more than about 20 per cent. of the total metal as iron the initial deposit contains relatively more nickel than does the electrolyte; for solutions containing a smaller proportion of iron the results are not quite definite, but it is probable that the deposits contain relatively more iron.

(5) The composition of the alloy of maximum iron content is also independent of the hydrogen-ion concentration of the solution; this deposit always contains relatively more iron than does the solution. The actual composition of this alloy may be affected by the total concentration of iron and nickel in the electrolyte and by stirring.

(6) The decrease in the iron content of the alloy after the maximum is reached is shown to be due to the impoverishment of the electrolyte in the vicinity of the cathode; this decrease is most marked when the rate of deposition of alloy greatly exceeds the rate of diffusion of ions to the electrode and is, consequently, greatest for solutions which are dilute or of low hydrogen-ion concentration.

(7) The apparently contradictory results of previous observers are discussed in the light of the information obtained in the present work.

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# THE DECOMPOSITION OF NITROUS OXIDE IN THE SILENT ELECTRIC DISCHARGE.

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A review of the literature relating to this subject showed the absence of any quantitative data regarding the behaviour of nitrous oxide when subjected to ionisation by collision in an electric discharge. The experiments now to be described relate to the behaviour of nitrous oxide when subjected to ionisation by collision due to alternating electrical fields of frequency 150 cycles per second. The electrical conditions, under which any particular experiment has been carried out, have been defined in most cases with respect to the potential applied to, and the current flowing through the reaction vessel.

## Description of Apparatus.

*The Source and Measurement of Electric Power.*—Single phase alternating current of frequency 150 cycles per second was delivered by a 1 K.W. rotary converter and was transformed up to the required voltage over the range 6000-12000 volts. The potential applied to the reaction vessel was measured by a Kelvin-White instrument and kept constant during a reaction within 1 per cent. by hand regulation of the resistance R, (Fig. 1), in the primary circuit of the transformer. The current flowing through the reaction vessel was indicated by a milliammeter of the dynamometer type. The power consumed in the reaction vessel was measured by noting the rise in temperature of a water-stream of known velocity, which was arranged to cool the electrodes of the reaction vessel. The rate of flow of the cooling water was adjusted to give a rise in temperature which could be read with an accuracy of about 1 per cent.

*Reaction Vessel.*—The gas exposed to the discharge was contained in the annular space between two coaxial glass tubes sealed together in the manner of a Siemen's ozoniser. The central tube was filled with mercury which formed one electrode. A glass jacket over the outer tube of the ozoniser filled with mercury constituted the other electrode. The inner electrode was cooled by immersing in it a thin walled glass vessel through which a stream of water was flowing; similarly the outer electrode was cooled by surrounding it with a jacket carrying a continuous stream of water. Separate streams of water, necessitating the use of two thermometers in each stream, were employed in order to obtain efficient cooling. At the entrance and the exit of the water cooler associated with the high tension electrode two short lengths of copper tube were inserted in the stream and connected to the high tension electrode. No appreciable current could therefore flow through the water in the cooling vessel. The thermometers reading the stream temperature were placed between the copper tube and the cooling vessel. This arrangement had the additional advantage that brushing from the high tension electrode to the cooling

vessel associated with it was eliminated. A third copper tube, connected to earth, was placed in the stream where it ran to waste, thereby ensuring a continuous and uniform load on the circuit.<sup>1</sup> The reaction vessel was of the following dimensions:—

Outer diameter of the outer tube . . . . .	2.60 cms.
Inner " " " " " " . . . . .	2.38 "
Thickness of the wall " " . . . . .	0.12 "
Outer diameter of the inner tube . . . . .	1.55 "
Inner " " " " " " . . . . .	1.33 "
Thickness of the wall of the inner tube . . . . .	0.12 "
Mean length . . . . .	33.9 "
Width of the annular space . . . . .	0.41 "
Volume of the annular space . . . . .	88.8 cc.
Capacity between surfaces of electrodes . . . . .	41.0 $\mu\mu\text{F}$ .
" " " " annular space . . . . .	44.3 "

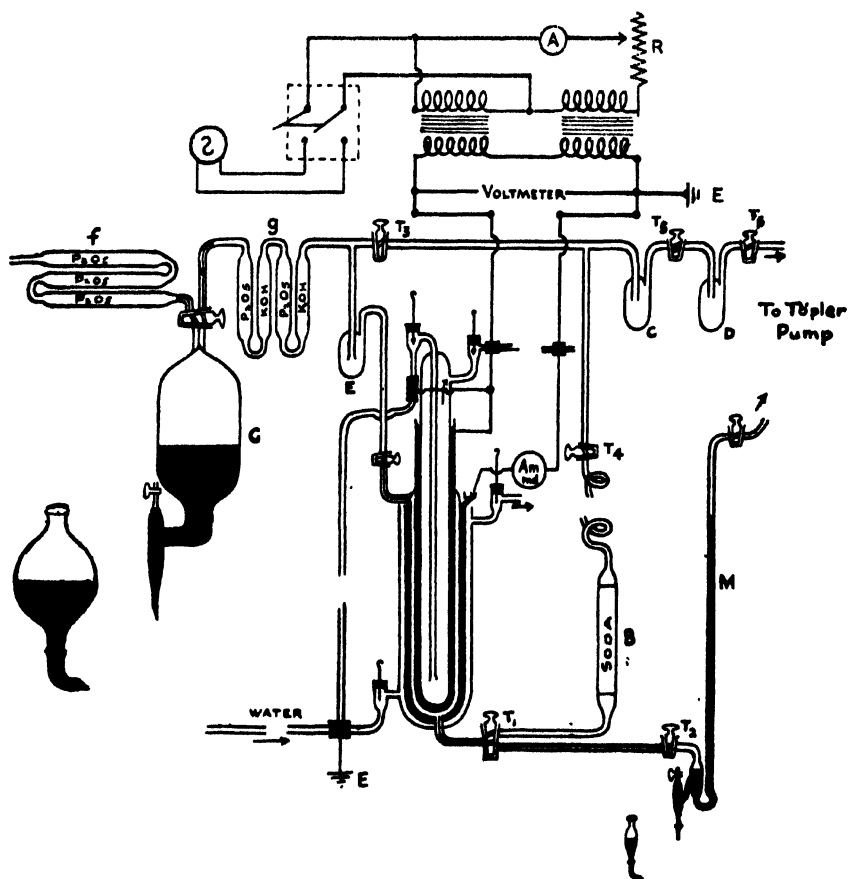


FIG. 1.

A general diagram of the apparatus and of the electrical connections is shown in Fig. 1. The reaction vessel is connected to a supply of nitrous

<sup>1</sup> For a discussion of this technique *cf.* Lunt, *Phil. Mag.*, 1926, 2, 314.

oxide stored in the gas holder G, to a mercury manometer M, and to a Töpler pump. The necessity of reducing to a minimum the volume of the gas not exposed to the discharge when making pressure measurements, and the rapid pressure changes developed during the reaction, made the use of a mercury manometer preferable to one of the glass spoon type. Considerable difficulty was experienced in avoiding the contamination of the mercury surface in the manometer by nitrogen peroxide and ozone. By opening the mercury sealed stopcocks  $T_1$ ,  $T_2$ , only when it was necessary to read the manometer, the fouling of the mercury was reduced to a minimum.

*Preparation of Gas.*—Nitrous oxide obtained from a cylinder was led through tubes *f*, containing powdered caustic potash and phosphorus pentoxide, to the gas holder G, and then slowly led through a further series of tubes containing potash, and phosphorus pentoxide, and condensed in the trap E, cooled by liquid air. At this temperature nitrous oxide freezes to a solid of negligible vapour pressure. Any volatile gaseous impurity, such as oxygen or nitrogen, can then be pumped out through the tap  $T_3$ . After removing the liquid air bath the first and the last fraction to vaporise were rejected, and the middle fraction was stored in the gas holder G. The purity of the gas was determined by the estimation of nitrogen and oxygen formed when it was completely decomposed by the discharge. It was found to be never less than 99.5 per cent. Before commencing an experiment the gas permanently stored over the drying and KOH tubes *g* was frozen out in the trap E by liquid air; the tap  $T_3$  was then opened to the Töpler pump to remove any traces of uncondensable gases.

*Analysis.*—The gases in the reaction vessel were pumped out through a tube B containing coarsely powdered caustic soda to remove nitrogen peroxide and nitrogen pentoxide. The use of potash was avoided on account of the action of potash on nitric oxide,<sup>2</sup> which might be present. The tube containing the crushed soda was fitted with ground joints to permit of its being readily recharged. Treatment of a solution of the soda, after exposure to the gases, by standard permanganate solution indicated in all cases that not more than traces of nitrite were present. The conversion to pentoxide of the peroxide formed in the discharge owing to presence of ozone is discussed later. After leaving the soda tube the gases were led through traps, C, D, cooled by liquid air. All volatile gases, nitrogen, oxygen and nitric oxide were then removed by the Töpler pump. These gases were tested for nitric oxide by means of acidified ferrous sulphate solution. In no case was the presence of nitric oxide observed at any stage of the reaction. The remaining mixture of nitrogen and oxygen was analysed by alkaline pyrogallol, the nitrogen being determined by difference. After the volatile gases had been pumped off, the liquid air vessels were removed and the unchanged nitrous oxide was collected over mercury by means of the pump. The gases were measured by means of a carefully calibrated constant volume gas burette, mounted in a water bath to ensure constancy of temperature.

### Experimental Results.

After the reaction vessel has been highly exhausted it was filled with nitrous oxide to a certain pressure; the gas was then exposed to the discharge at a constant voltage, for a definite period, and the resulting decomposition mixture was pumped out and analysed. Two principal series of experiments have been carried out, one in the pressure range

<sup>2</sup> Barnes, *J. Soc. Chem. Ind.*, 1926, 45, 259.

20.0-41.0 cms. Hg, at 6750 volts (r.m.s.), and the other in the pressure range 42.0-82.0 cms. Hg, at 12,400 volts (r.m.s.).

In the earlier experiments, the data for which are given in Fig. 2, the analysis of the decomposition products was carried out in the following way. Immediately after the cessation of the discharge, the tap  $T_4$  was closed, the mixed gases were allowed to flow into the evacuated soda tube and remained in contact with soda for about twenty minutes. Experience has shown that this time was sufficient for the complete absorption of any acidic nitrogen oxides. The taps  $T_1$ ,  $T_6$  were then closed and the mixture in B was admitted to C by opening  $T_4$ ; after the gases had been allowed to remain in C for about five minutes,  $T_4$  was closed and  $T_6$  opened. At the end of a similar interval,  $T_6$  was opened and the gases between  $T_4$  and  $T_6$  were pumped out, after passing through a further length of soda tube. This process was repeated till all the volatile gases were pumped out and

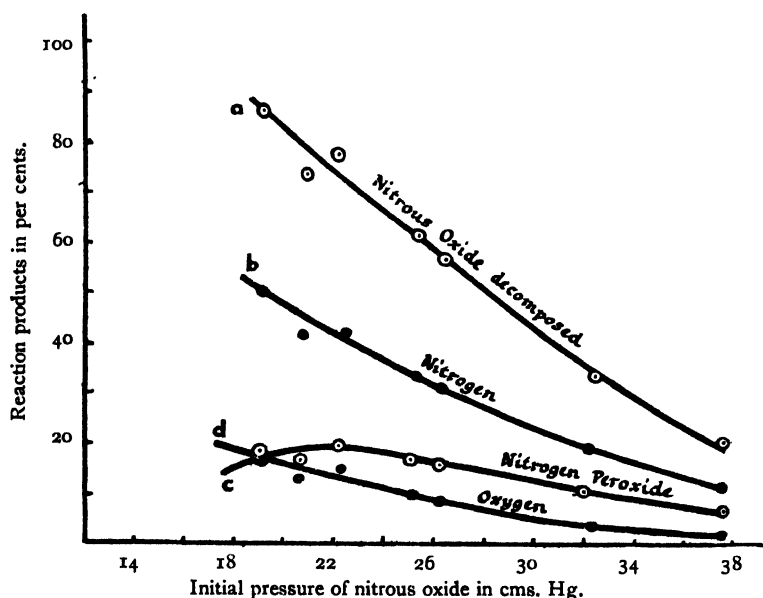


FIG. 2.—Voltage = 6750 (r.m.s.). Time of exposure = 10 mins.

analysed in the manner already described. A slight fouling of mercury in the Töpler pump indicated the presence of ozone in the decomposition mixture. The low yields of nitrite in the soda tube may be explained by the conversion by ozone of some of the peroxide to pentoxide; this is a well-known method for preparing nitrogen peroxide from peroxide. The amounts of peroxide (inclusive of pentoxide in the decomposition mixture which was also absorbed by alkali), which are plotted in Fig. 2, have been calculated in the following way:—

Let  $P_{N_2O}$  and  $V$  be the initial gas pressure and volume of the annular space respectively, then  $a$ , the mass of  $N_2O$  exposed to the discharge is given by:—

$$a = \frac{P_{N_2O} \times V \times 44}{RT}$$

Similarly,

$$= \frac{P_{O_2} \times V_{O_2} \times 32}{RT}$$

gives the mass of the free oxygen in the final mixture where,  $V_{O_2}$  is the volume of oxygen collected at the pressure  $P_{O_2}$ . The results in Fig. 2 have been expressed in terms of the mass percentage of the free oxygen formed,  $100\beta/a$ . The amounts of nitrogen and of undecomposed nitrous oxide have been similarly reckoned and plotted. The sum of the values for the last three constituents, subtracted from 100, gives the corresponding value for the peroxide present. The results of the first series of analyses of the decomposition mixture at 6750 volts and with a constant time of exposure to the discharge (10 minutes), have been plotted in Fig. 2.

The shape of the curve for peroxide (cf. curve *c*, Fig. 2) is interesting. It was first thought to be due to experimental error; later experiments have confirmed it and is to be anticipated from the considerations regarding the mechanism of the reaction to be discussed later.

The observation of the presence of ozone and, therefore indirectly, of nitrogen pentoxide, led to the following alteration in the method of the analysis of the gaseous mixture, which was adopted in all subsequent

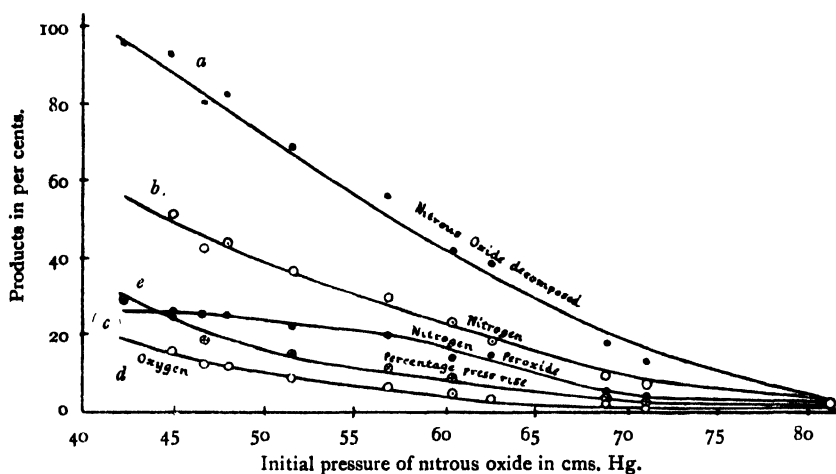


FIG. 3.—Voltage = 12,400 (r.m.s.). Time of exposure = 1 hour.

experiments. Daniels, Wolf, and Karrer<sup>3</sup> have shown that nitrogen pentoxide in the presence of peroxide decomposes slowly to nitrogen peroxide and oxygen. The mixed gases were therefore allowed to stand for about twelve to fifteen hours before being pumped out for analysis. This time considerably exceeds that necessary to effect the transformation of any ozone and nitrogen pentoxide into oxygen and nitrogen peroxide. Ozone was not observed in the mixture after this.

The results of analysis, obtained by the above-mentioned procedure, of the decomposition mixture under 12,400 volts and for a constant time of one hour of exposure to the discharge at varying initial pressures are plotted in Fig. 3.

The curves shown in Figs. 2 and 3 show the rapid diminution of the degree of decomposition with increase of the gas pressure. For example, at 12,400 volts the amount of nitrous oxide decomposed falls from 96.0 per cent. to 2.3 per cent. as the initial pressure is increased from 42.2 to 82.4 cms. Hg. (cf. curve *a*, Fig. 3). Since the time of exposure of the gas

<sup>3</sup> *J. Amer. Chem. Soc.*, 1922, 44, 2402.

to the discharge was maintained constant, it is clear that the mean rate of decomposition diminishes much more than linearly with respect to pressure. Similar results have been observed regarding the initial rate of decomposition and will be presented in a later communication.

From the results of the analyses, shown in Figs. 2 and 3 and Table I., it is clear that the nature of the decomposition products is independent of the gas pressure; the latter merely slows down the rate of the reaction and the mixture, obtained at an increased gas pressure, corresponds to that at an earlier stage of decomposition at a smaller pressure. The results of analysis using the highest (82.4 cms.) and lowest (42.2 cms.) pressure, therefore, represent the decomposition mixtures, respectively, at the earliest and the final stage of one and the same reaction; results with pressures between the extreme values correspond to intermediate stages of decomposition. Thus regarded, the results of analysis are readily interpreted in general and also in relation to a possible mechanism of the reaction suggested later. On examining the amounts of nitrogen and oxygen in both the series of experiments, it is seen that the ratio of nitrogen to oxygen, expressed in mols., rises continuously as the earlier stages of decomposition are examined,

TABLE I.

VOLTAGE APPLIED TO OZONISER = 12,400 VOLTS (r.m.s.).  
TIME OF EXPOSURE TO DISCHARGE = 1 HOUR.

Initial Pressure in cms. Hg.	42.2	44.8	47.85	51.55	56.9	60.5	62.4	68.75	71.1	82.4
Percentage of N <sub>2</sub> O decomposed	96	93.3	82.1	67.2	54.5	42.0	38.7	17.1	13.3	3
Ratio $\frac{N_2}{O_2}$ in mols.	3.3	3.6	4.4	4.8	5.1	4.8	5.2	5.1	6.1	15.7

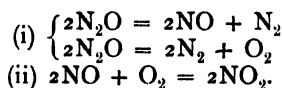
*i.e.* in the decomposition mixtures at higher pressures of nitrous oxide. One such series of results has been tabulated here from data presented in the curves for nitrogen and oxygen in Fig. 3.

The increase in the ratio is abrupt in the last vertical column. Associated with this, the reduction in the percentage decomposition of nitrous oxide is also abrupt. In a corresponding way the velocity of the reaction at higher pressures has been found to diminish rapidly. The velocity was determined (i) approximately from the initial slope of the pressure-time curves (*cf.* Figs. 4 and 5), and (ii) comparatively more accurately from an analysis of the decomposition mixture after an exposure of two minutes to the discharge with a different ozoniser. A further discussion of these results is reserved for a later communication. Results obtained in the series of experiments at 6750 volts (*cf.* Fig. 2), gave similar values for the ratio of nitrogen to oxygen and, therefore, need not be tabulated.

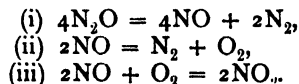
A number of experiments were made regarding the nature of the final products of decomposition, at values of initial pressure varying from 24.6 to 46.2 cms. under a constant potential of 12,400 volts. It was found that the final state corresponded to complete decomposition of nitrous oxide, giving a mixture of nitrogen and oxygen in the volume ratio 2 : 1. The amounts of nitrogen and oxygen in the final mixture agreed, within 0.5 per

cent., with the initial amounts of nitrous oxide. The conclusion that the final state corresponds with complete decomposition of nitrous oxide into nitrogen and oxygen and that this is independent of the potential applied to the reaction vessel has been confirmed by experiments on mixtures of nitrogen and oxygen in the ratio 2 : 1. A mixture produced by complete decomposition of nitrous oxide was exposed to the discharge at 6300 volts for seven hours. No change whatever was observed in the gas. In another experiment the mixture at a total pressure of 70.15 cms. Hg. was subjected to the discharge at 6300 volts and subsequently at 12,400 volts for a period of several hours. Again no change was observed. In all the above experiments, the final mixture after the completion of the decomposition was found to be free from peroxide. It is clear that no further reaction is induced by exposure of the final nitrogen oxygen mixture to the discharge for a period of several hours. Peroxide observed at any stage of the decomposition is therefore to be regarded as an intermediate product of the decomposition of nitrous oxide. If it be assumed that the decomposition is represented by the two following consecutive reactions,  $4\text{N}_2\text{O} = 3\text{N}_2 + 2\text{NO}_2$ , and  $2\text{NO}_2 = \text{N}_2 + 2\text{O}_2$ , of which the latter is the less rapid, then it is possible to explain the large proportion of nitrogen observed (*cf.* Table 1.) in the initial stages of the reaction, its gradual decrease as the reaction proceeds and the formation of nitrogen peroxide as an intermediate product. Peroxide has been observed by Wourzel<sup>4</sup> in the decomposition of nitrous oxide by  $\alpha$ -particles, and the work of Briner, Meiner, and Rothen<sup>5</sup> has shown that in the thermal decomposition of nitrous oxide as much as 25 per cent. is converted into nitric oxide. It is possible, therefore, that the initial stage in the decomposition of nitrous oxide in the discharge, resulting in the formation of nitrogen peroxide, may be represented by either of the groups of reactions, *a*, *b*. :-

(*a*) Two simultaneous reactions (i), followed by (ii).



(*b*) Three consecutive reactions (i), (ii) and (iii).



Some additional and independent evidence is needed to decide definitely between the two possibilities. It is, however, to be anticipated that the group of reactions (*b*), would correspond to a higher concentration of nitric oxide during the initial stages of the decomposition, if it be supposed that the reaction, (*b*, i) is more rapid than (*b*, ii). The fact that nitric oxide was never observed and that free oxygen was observed at all stages of the reaction, suggests that probably, (*b*) does not represent the mechanism of the decomposition of nitrous oxide under the experimental conditions in this work. So far as the general experimental results are concerned, it is sufficient to regard the total decomposition as consisting of the two consecutive reactions referred to above, peroxide being the intermediate product. A further confirmation of this point is afforded by the similarity to be found between the curve *c*, relating to the peroxide, in Figs. 2 and 3,

<sup>4</sup> *Le Radium*, 1919, 11, 289, 332.

<sup>5</sup> *Helv. Chem. Acta.*, 1926, 9, 409.

and that usually characteristic of an intermediate product in a series of consecutive chemical reactions.

In a further investigation shortly to be published on this subject, relating to the mechanism of decomposition, the results of the analyses of the reaction mixtures at successive stages of the decomposition of one and the same reaction at a given initial pressure have confirmed the deductions previously made regarding the nature of the reaction, and particularly the conclusion that the decomposition mixtures (Figs. 2 and 3) obtained with varying gas pressures represent successive stages in time in the course of one and the same reaction; and further that the curve for peroxide shows a maximum similar to that in the corresponding curves in Figs. 2 and 3.

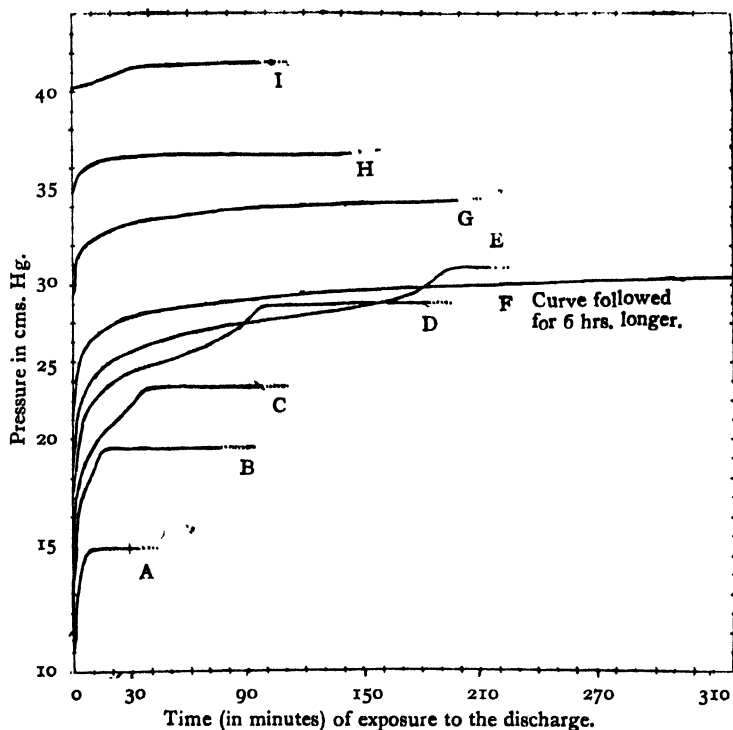
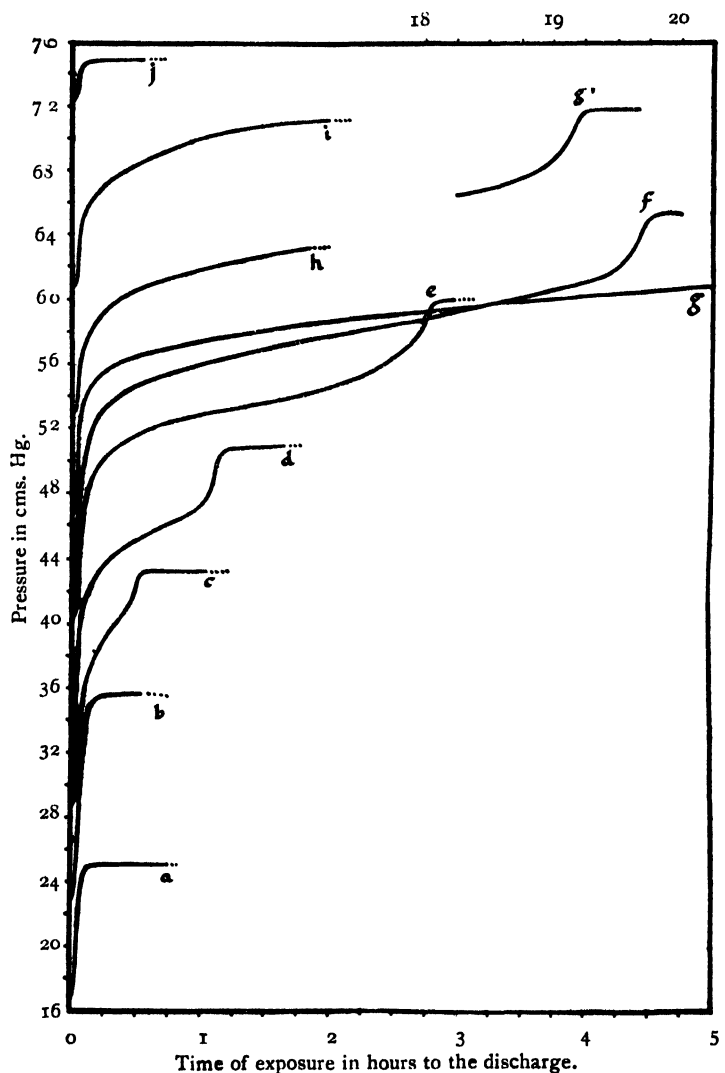


FIG. 4.—Voltage = 6300.

### Pressure and Current Variation during Decomposition.

The course of the reaction was followed by measuring the pressure of the reaction mixture, adjusted to a constant volume, from the instant of the application of the potential to the reaction vessel. It was found that in spite of the arrangement for cooling the electrodes (*cf.* Fig. 1) the temperature effect of the glow in the gas was not completely eliminated; the pressure measurements are therefore subject to an undetermined correction on that account. Two series of experiments have been carried out, one in the pressure range 11.0 to 41.0 cms. Hg., at 6300 volts, and the other from 16.0 to 82.0 cms. Hg., at 12,400 volts. Pressure measurements were taken until the completion of decomposition, as judged by the absence of further rise in pressure. The final pressure was recorded after the ozoniser was allowed to cool; the pressure rise observed at the end of the reaction varied

from 47 to 49 per cent.; the theoretical pressure rise is 50 per cent. The discrepancy is due to the undecomposed gas in the dead space between the reaction vessel and the manometer. The conclusion that the final products are nitrogen and oxygen in the required stoichiometric ratio, based on the results of analysis in which error due to the dead space was



$g'$  is the final stage of the curve  $g$ , times being shown on the top line.

FIG. 5.—Voltage = 12,400.

avoided has been previously mentioned (*cf.* p. 232). The results of these experiments are shown by curves A-I (Fig. 4) and a-j (Fig. 5). In some cases at higher pressures [*cf.* curves F-I (Fig. 4) and h-j (Fig. 5)], the pressure rise became too slow to allow the course of the reaction to be followed to completion.

The chief fact brought out by the results represented in Figs. 4 and 5 is

the very rapid increase in the time for total decomposition of the gas as the initial pressure is progressively increased. Thus in Fig. 5 at 12,400 volts the time for the total decomposition rises from 6 minutes to about 19 hours, as the initial pressure is raised from 16.65 cms. to 47.0 cms. Hg.

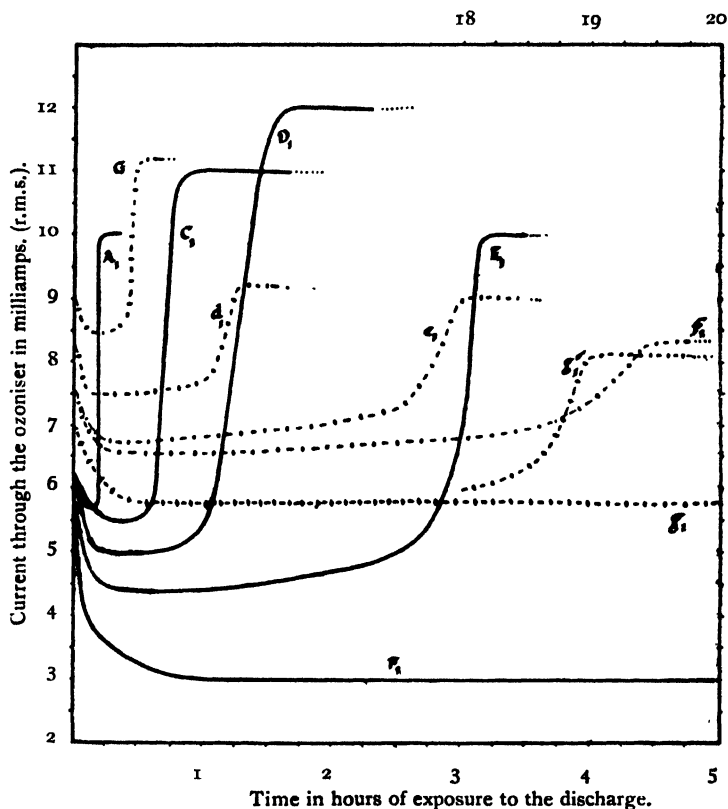
It will be noticed that each curve possesses three characteristic portions. The first associated with a steep gradient, corresponds to the initial stage of the decomposition. The second part, in which the gradient is diminished and becomes almost zero over an interval of several hours at the higher pressures, suggests the intervention of a new factor which retards the reaction. A yellowish brown coloration due to peroxide is perceptible at the beginning of this stage and becomes increasingly prominent. The final section is characterised by a sudden increase in the gradient, followed by a diminution to zero, concomitant with the completion of the decomposition. The characteristics of these curves vary in a notably systematic manner with the initial pressure of nitrous oxide. As this pressure increases, the large initial gradient diminishes, for example it becomes almost zero in curve I (Fig. 4) for the initial pressure of 40.35 cms.; the intermediate stage rapidly increases in duration, and the final increment of pressure, although increasing in magnitude, becomes less sudden. The curves for higher pressures in Figs. 4 and 5 have not been completed as the time required for the completion of the decomposition is excessively large. It must be stressed that equilibrium has not been attained at the stages corresponding to the apparently horizontal part of these curves. To mention a specific case: in Fig. 5, curve *h*, at the initial pressure of 52.7 cms. at 12,400 volts, the rise in pressure at the end of the first 8 hours was 24.3 per cent.; this increased to 26.3 per cent. and 27.7 per cent. at the end of 35 and 54 hours respectively. The time for the remaining 22.3 per cent. of pressure rise necessary to reach the 50 per cent. pressure rise corresponding to the completion of decomposition will be correspondingly large since the reaction is in progress though at a very small rate.

The effect of voltage in increasing the speed of the reaction has been already noticed in connection with the results of analysis. One typical case may be mentioned from the results shown in the pressure-time curves; the curve F in Fig. 4, which is not completed, refers to decomposition at an initial pressure of 23.3 cms. at 6300 volts; exposure to the discharge for 13 hours gave a pressure rise of only 31.8 per cent., the rise during the last six hours being 2.1 per cent. only. The time for the completion of the reaction corresponds to 50 per cent. pressure rise. On repeating the above experiment with nearly twice the previous voltage (*i.e.* 12,400) and at the same gas pressure, the decomposition was complete in 14 minutes as shown by curve *b* (Fig. 5). It may therefore be stated generally that the velocity of the reaction increases with the potential applied to the reaction vessel and diminishes as the gas pressure increases.

It was found that the current flowing through the reaction vessel varied with the stages of the decomposition of nitrous oxide.

It is interesting to compare the curves in Fig. 6, showing the variation of the current during the progress of the reaction at different initial pressures, with the corresponding pressure-time curves (Figs. 4 and 5). In these two series, each of the pairs of curves, *aa'*, *bb'*, *cc'*, and so on, relates to the decomposition at a given initial pressure which is to be considered as the variable parameter of the series. A comparison of the two sets of curves reveals a close similarity. The three characteristic portions of the pressure time curves correspond, on the time axis, to three equally well-defined sections of the current-time curves at constant voltage. In the initial stage

the current diminishes; in the intermediate stage the gradient is practically zero; and in the final stage the current increases up to a constant value corresponding to complete decomposition. It must be explained that the current values recorded in these curves refer, not to the true current flowing through the reaction vessel but to the sum of this current and that flowing through the cooling water system. Since this latter is sensibly constant the



Variation of the Current during the Decomposition.

— 6300 Volts.

..... 12,400 Volts.

Curve A<sub>1</sub> for pressure = 14.7 cms.

Curve G for pressure = 27.8 cms.

" C<sub>1</sub> " " = 16.5 "

" d<sub>1</sub> " " = 33.1 "

" D<sub>1</sub> " " = 19.4 "

" e<sub>1</sub> " " = 40.4 "

" E<sub>1</sub> " " = 20.1 "

" f<sub>1</sub> " " = 42.1 "

" F<sub>1</sub> " " = 23.3 "

" g<sub>1</sub> " " = 47.0 "

" g'<sub>1</sub> " " = final stage of curve g<sub>1</sub>.

FIG. 6.

curves can be considered as representing the changes of current related to the decomposition of nitrous oxide.

An account of the measurement of the energy developed as heat in the reaction vessel during the course of a reaction will be communicated later. Preliminary experiments have shown that the final rise in current is accompanied by an increase in the power expended in the reaction vessel. For instance with an initial pressure of 46.4 cms. Hg. at 12,400 volts, the heat developed during the intermediate stage of decomposition was  $6 \pm 5$  watts;

the watts observed upon the completion of decomposition were  $16.0 \pm 1$ . It would thus seem that the results shown in Fig. 6 giving the variation of current as related to the stages of decomposition of nitrous oxide, are to some extent confirmed by the energy measurements. This variation of the conducting properties of an ionised gas forms a very interesting class of new phenomena which is being investigated in detail.

### Summary.

(1) The decomposition of nitrous oxide by the silent electric discharge has been studied in the pressure range 11.0-82.0 cms. Hg and under 6000-12,500 volts (r.m.s.). Results of the analysis of the decomposition mixture at different stages of the reaction are given.

(2) The decomposition goes to completion giving a mixture of nitrogen and oxygen. The nature of the final products is independent of the potential applied to the reaction vessel, and of the gas pressure. Nitrogen peroxide occurs as an intermediate product of this decomposition for which a mechanism has been suggested.

(3) The time for the total decomposition increases very rapidly with increase in the gas pressure. The mean rate of the decomposition increases with increase in the potential applied to the reaction vessel and diminishes as the gas pressure increases. A close similarity has been observed between the variation of the current flowing through the reaction vessel and the phases of the decomposition as judged from the shapes of the pressure-time curves. The rise in the current upon the completion of the decomposition is accompanied by an increase in the power consumed in the reaction vessel.

In conclusion the writer welcomes this opportunity of expressing his indebtedness and thanks to Messrs. Brunner, Mond & Company, and to Messrs. Metropolitan Vickers Electrical Company for loan of apparatus; to Dr. R. W. Lunt for much valuable help, and especially to Professor F. G. Donnan, F.R.S., at whose suggestion this work was undertaken, for his instructive advice and kind encouragement throughout the course of this work.

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## A RECORDING HYDROSTATIC BALANCE OF SIMPLE DESIGN.

BY F. G. TRYHORN AND W. F. WYATT.

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Various devices have been used to record automatically progressive increments or decrements of weight, especially in the study of the adsorptive powers of textile fibres and of porous substances. Most of these devices<sup>1</sup> involve the periodic automatic addition to one balance pan of small weights or shot, to compensate a corresponding increase in weight of the other pan. By using suitably small units of weight it is possible to reduce to any de-

<sup>1</sup> Odén-Keen, *Trans. Far. Soc.*, 1922, 17, 326; *Proc. Roy. Soc.*, 1924, 106A, 33.

sired minimum the vertical displacement of the balance pans between successive additions. This is of particular importance in studying the velocity of adsorption and in measuring diffusion coefficients, in order to maintain as constant as possible the distance between the adsorbent and the bulk adsorbate. The mechanical arrangements to secure this end are, as a rule, complicated and, if a somewhat larger vertical displacement of the balance pan is permissible, it is possible to adapt a simple hydrostatic compensation balance to the purpose. The balance to be described is of this type and is suitable for measurements of total adsorptive power, of the velocity of adsorption, and, with slight modifications, for the determinations of diffusion coefficients. For the latter purpose a moderately long path between the adsorbent and the liquid of which the vapour is to be adsorbed must be maintained.

The apparatus is essentially one which may be used in conjunction with any ordinary balance. A uniform, cylindrical rod A, of glass or metal, hangs by a fine platinum wire B, from the right-hand arm of the balance at such a height that it is partly immersed in a non-volatile liquid C. The vessel D containing this liquid is jacketed so that the contents may be kept at constant temperature by the circulation of water from a thermostat through the jacket. A wooden bridge spanning the balance pan supports the jacketed vessel. A second platinum wire E, attached to the same arm of the balance, rotates, with any movement of the balance-beam, by a lever F, a concave mirror G, suspended on a separate brass stand H. This stand is provided with levelling screws for centring and adjusting the mirror. The mirror carrier J, of brass, is pivoted on two tungsten steel needles, which rest vertically in an agate cone and trough cemented on the brass stand. The mirror, which is mounted so that the centre of the reflecting surface is in line with the points of the needles, is of highly polished stainless steel, 1 cm. in diameter and 50 cms. in focal length. A small V-shaped bend near the free end of the lever F rests in a hook at the end of the wire E. Experience shows that this bearing is practically frictionless and without slip: it transmits oscillations of the balance beam to the rocking mirror without any apparent damping. Movements of the mirror are recorded photographically by means of a spot of light reflected from the mirror on to a rotating vertical drum carrying a strip of rapid bromide paper. The drum is carried on the spindle of a gramophone motor in which an electromagnetic drive has been substituted for the usual spring. The magnet operating the drum mechanism is energised periodically by impulses transmitted from a clock worked by an electrically driven second pendulum. Contacts are placed on the minute wheel of the clock and on the pendulum so that impulses may be transmitted at intervals of 2, 15, 30, or 60 secs., causing a complete rotation of the drum in 1.25, 9.375, 18.75, or 37.5 hours. Two small electric lamps with pin-hole shutters are used, the one to provide the reflected beam from the mirror, and the other to place a time mark at fixed intervals on the record. The arrangement of the contacts on the clock allows the former to give either continuous illumination, or (in lengthy adsorption experiments) a flash every two seconds, and the latter to give time marks at intervals of 0.5, 1.0, 7.5, 15, or 30 minutes. It will be seen from the diagram (Fig. 1) that if the balance is so poised that the left-hand pan is lighter than the right, any increase in weight on the left-hand pan will lift the plunger partly from the liquid, thereby setting up a hydrostatic compensation of the increment in weight. At the same time the lever F will be lifted, causing a partial rotation of the mirror and a downward, vertical displacement of the spot of light on the

recording drum. Any increase in weight in the left-hand balance pan becomes thus automatically compensated by the partial withdrawal from the liquid of the plunger. If we neglect the density of the air, it is clear that during this withdrawal the effective weight of the plunger increases by a weight equal to that of the liquid replacing the volume of the portion of the plunger withdrawn. The range of the balance is determined by the radius  $r$  of the plunger, the density  $d$  of the immersion liquid, and by the vertical displacement  $h$  of the balance pans during a complete swing of the balance. The weight of liquid replacing the portion of the plunger withdrawn during a complete swing is then  $\pi r^2 h d$ , and represents the effective range of the balance under these conditions. The balance at present in use is one of the long beam type made by Verbeek and Peckholdt; a complete swing of the balance corresponds with a vertical displacement of the pans of 0.60 cm. The liquid used is the fraction of a paraffin oil boiling 250–260° C., and of density 0.8352 at 20° C. The rod in use has a radius

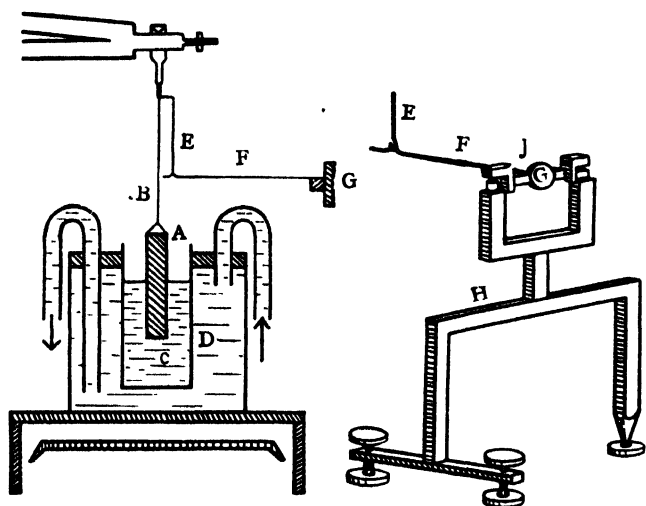


FIG. 1.

of 3.18 mms. Using these values the range of the balance is 0.1592 gm. By using a rod 1 cm. in radius and, as the immersion liquid  $\beta$ -brom naphthalene,  $d_0$  1.605, the range is increased to 3.026 gms.

It has been found that in prolonged experiments a small correction must be introduced for the slight evaporation of the immersion liquid which occurs at 20°, the temperature of the circulating water. A fall in the level of this liquid through evaporation will produce an apparent loss of weight in the left-hand pan. For the paraffin fraction mentioned above this correction has been found to be 0.096 mgm. per hour. This rate of loss has been shown to be constant over periods of 48 hours. This correction must therefore be added to the recorded weights.

The effect of temperature variations may be calculated from the coefficient of cubical expansion of the immersion liquid. A rise in temperature will cause a decrease in the density of the immersion liquid and, therefore, the movement of the plunger to compensate a given increase in weight of the left-hand pan will be enhanced. For the paraffin the temperature correction, 0.073 per cent. per 1° C., has been confirmed by experiment.

In practice, with a thermostat adjusted to  $\pm 1/25^\circ \text{C.}$ , the error due to temperature fluctuations becomes less than 0.003 per cent. of the recorded weight. The length of the lever F, and the distance from the mirror of the rotating drum are so adjusted that a movement of the balance-beam corresponding with a complete swing of the balance causes a vertical displacement of the spot of light on the drum of 14 cms., or 1 cm. less than the width of the bromide paper in use.

### Calibration of the Balance.

Experience has shown that equal increments of weight on the left-hand pan cause equal downward vertical displacements of the spot of light on the recording drum. It is, however, desirable to calibrate the balance at the beginning of each experiment, before the drum mechanism is started. This is done by placing successively increasing weights on the left-hand balance pan and making a brief exposure on the recording drum by momentarily switching on the recording lamp when the balance has taken up a position of equilibrium. To verify the reversibility of the balance it is usual to make a second series of calibration marks in descending order of weight, after the drum has been slightly rotated. The two series of marks should form two parallel vertical rows of dots if the balance is properly adjusted. The following example of an analysis of a set of calibration marks may be cited:—

Weight on left-hand pan. (gm.)	0.0	.01	.03	.05	.07	.09	.11	.13	.15
Distance between marks. (mms.)	9.0	18.0	17.5	17.5	17.5	17.5	17.3	17.4	

The mean displacement is 8.78 mms. per 0.01 gm. increase in weight. The maximum variation over an interval of 0.02 gm. is 0.44 mm., and the average variation  $\pm 0.14$  mm. This would, for a range of 0.1592 gm., introduce an error of 0.158 mgm.

### The Determination of Adsorptive Power, of Velocity of Adsorption, and of Diffusion Coefficients.

These measurements may be conveniently made by means of the apparatus shown in Fig. 2. A jacketed, annular vessel is supported clear of the balance pan by a wooden stand. The central hole is closed by a cork carrying a glass tube with a fine aperture at the upper end. A light brass pan is suspended from the balance arm by a fine wire passing through this aperture, so that the centre of the pan is slightly above the upper edge of the annular space when the balance pan is fully raised. A gram weight is placed in the brass pan, and weights are then added to the right-hand balance pan until the beam takes up an equilibrium position with its pointer 9 divisions to the left of the scale zero. The balance is then calibrated by the method described above. The gram weight is replaced by a gram of adsorbent material,

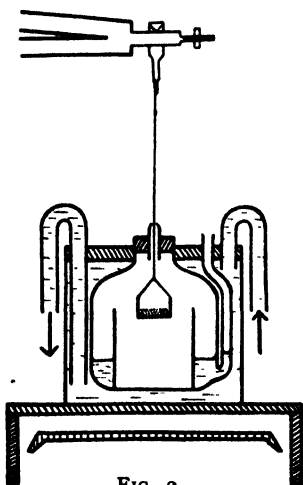


FIG. 2.

and 25 c.c.s of the liquid of which the vapour is to be adsorbed are run into the annular space. The drum mechanism is then started and the recording and time-marking lamps switched on. After adsorption is complete, an analysis of the photographic record, in conjunction with the calibration and time marks, enables a computation to be made of the total amount of vapour adsorbed, and of the velocity of adsorption at any moment. It may be mentioned that measurement of the adsorption of saturated vapours by charcoal by this method confirms quantitatively the results previously obtained by the method of direct weighing.<sup>2</sup> The diffusion coefficients of the vapours may be calculated by the method of Mack<sup>3</sup> with a moderate degree of accuracy. This is possible since by the introduction of the annular space the distance between the surfaces of the volatile liquid and the adsorbent changes during the adsorption of 0.02 – 0.04 gm. of vapour by not more than 0.7 per cent.

In conclusion it may be mentioned that since this balance was constructed the hydrostatic compensation method has been used by Guichard.<sup>4</sup> His method, consisting in compensating changes in weight by adding or withdrawing by a burette sufficient immersion liquid to restore the balance to its original equilibrium, is more laborious than ordinary weighing and cannot be made automatic or self-recording.

### Summary.

An automatic recording balance, working on the hydrostatic compensation principle is described, and its application to the measurement of adsorptive power, velocity of adsorption, and diffusion coefficients is indicated.

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## INVESTIGATIONS ON GASEOUS EXPLOSIONS. PART II. IONISATION IN DETONATING AND NON-DETONATING MIXTURES OF HYDROGEN AND OXYGEN.

By S. W. SAUNDERS.

*Received January 22nd, 1927.*

In Part I.<sup>1</sup> it was shown that the electrical conductivity of the hot gases produced in explosions of hydrogen and oxygen is mainly caused by the thermal ionisation of the molecules in the gaseous mixture. The electrical conductivity of a volume of exploding gas should therefore be dependent on any of those factors which modify its temperature.

The maximum temperature attained by a given volume of gas during an explosion is a function, not only of the heat of reaction and the specific heat of the gases, but also of the time which elapses before the gas is completely burnt. The longer this time, the greater the loss of heat by

<sup>2</sup> Tryhorn and Wyatt, *Trans. Far. Soc.*, 1926, 22, 134.

<sup>3</sup> Mack, *J. Amer. Chem. Soc.*, 1925, 47, 2468.

<sup>4</sup> Guichard, *Bull. Soc. Chim.*, 1926 (iv.), 39, 1113.

<sup>1</sup> *Trans. Faraday Soc.*, 22, 324, 1926.

radiation to the walls of the explosion vessel. Consequently, high speeds of explosion are accompanied by high maximum temperatures, and, if the above thesis be correct, by relatively high degrees of ionisation in the gaseous mixture.

From the experiments of Dixon on the velocity of sound waves in the hot products of gaseous explosions, it is clear that the temperature in the wave front may exceed the calculated temperature of explosion very considerably. This is very marked in the detonation wave, where the temperatures are raised by adiabatic compression. It follows, therefore, that the degree of ionisation in a detonating mixture should be higher than for a mixture which has not reached that stage of combustion.

With an Einthoven galvanometer (of period  $1/350$  sec.) as a recording instrument for the measurement of electrical conductivity, it is doubtful if any effect during the actual passage of a detonation wave could be perceived, but an idea of the conductivity of the gases after the detonation wave has passed can be obtained. One of the consequences of detonation should, however, be detectable, since, on account of the rapid combustion of the gaseous mixture, there is a relatively small loss of heat by radiation in the initial stages of the explosion and hence a high temperature of explosion and a high degree of ionisation will be attained.

In this paper experiments are described in which changes in the rate of explosion were brought about by increasing the length of travel of the explosion wave before it enters a spherical explosion vessel. The anticipated relationship between the velocity of explosion and conductivity is shown to be present; the conductivity of a given gaseous mixture increases with increase in the rate of explosion.

The effect of the addition of "anti-knocks" and "knock inducers" under these conditions has also been studied.

### Experimental.

The conductivity of gaseous mixtures of hydrogen and oxygen exploding at varying speeds has been measured with the apparatus previously described.<sup>1</sup> Firing tubes of different lengths were fixed to the spherical bomb in such a manner that the explosion wave travelled different distances before it ignited the gases in the bomb, where its electrical conductivity was measured. The ejection of the gases produced in these tubes into the gases in the bomb set up a degree of turbulence which varied with the composition of the mixture and the length of the tube. The variation in the speed of explosion of the gases in the bomb was thus due partly to variations in turbulence and partly to variations in the velocity of the explosion wave.

The bomb itself, including the arrangement of the electrodes, has been described previously.<sup>1</sup> The thick walled brass firing tubes, of lengths 1, 2, 4 and 6 feet, were screwed into the place normally occupied by the firing plug. By this means the gas could be fired either close to the walls of the bomb or at a distance of 1, 2, 4 or 6 feet from the walls. The internal diameter of the firing tubes was 15 mms., which is well above the minimum size which Dixon found was necessary to allow of the formation of the detonation wave.<sup>2</sup>

With this arrangement, in which the volume of the bomb is 1800 c.cs. and that of the longest firing tube is 320 c.cs., the gases in the bomb itself remain approximately at atmospheric pressure at the instant they are fired.

<sup>2</sup> *Phil. Trans.*, 184 A, 97, 1893.

In the extreme case, with the mixture  $2\text{H}_2 + \text{O}_2$ , owing to the explosion in the tube, nearly 300 c.cs. of gas will be expelled into the bomb when the explosion wave is just entering, so that the initial pressure of the bomb gases at the moment of firing will be 1.17 atmospheres. The value for the current passing between the electrodes can be corrected for this small increase in pressure, since it has been found that the current carried by the exploding gases is directly proportional to the initial pressure.<sup>1</sup> In the

TABLE I.

Mixture.	Length of Firing Tube. Feet.	$10^4$ C. Amps.	Equation for $10^4$ C. Amperes.	$dC/dd$ .
$6\text{H}_2 + \text{O}_2$	2	0.88	$0.36 + 0.13 d$ .	0.13
	1	1.10		
	6	1.20		
	4	0.86		
	0	0.36		
$4\text{H}_2 + \text{O}_2$	0	3.0	$2.0 + 3.5 d$ .	3.5
	2	13.0		
	6	18.0		
	4	20.0		
	1	15.0		
$3\text{H}_2 + \text{O}_2$	0	15.0	$11.0 + 13.2 d$ .	13.2
	2	40.2		
	4	52.1		
	6	85.9		
	1	28.8		
$2\text{H}_2 + \text{O}_2$	0	38.2	$30 + 22.7 d$ .	22.7
	4	106		
	2	90		
	1	60		
	6	174		
$\text{H}_2 + \text{O}_2$	0	24	$20 + 12.0 d$ .	12.0
	2	54		
	4	77		
	1	38		
	6	93		
$\text{H}_2 + 1\frac{1}{2}\text{O}_2$	0	10	$7.5 + 7.1 d$ .	7.1
	2	21		
	4	42		
	6	47		
	1	19		
$\text{H}_2 + 2\text{O}_2$	0	1.6	$0.8 + 2.8 d$ .	2.8
	2	7.1		
	4	10.8		
	6	17.8		
	1	4.3		

results which follow, this correction for pressure has been made for each experiment.

If it is assumed that, in the extreme case, this compression to 1.17 atmospheres is adiabatic, the rise in temperature is only of the order of  $10^\circ \text{C}$ ., so that no great error will be introduced if this factor is ignored.<sup>1</sup>

The results are comparable with each other and with those of the preceding series, but they suffer from the objection that, although the gas in the firing tubes may be detonating, detonation may not take place in the

bomb owing to the considerable increase in the diameter of the explosion vessel when the detonation wave emerges from the tube into the bomb.

### Results.

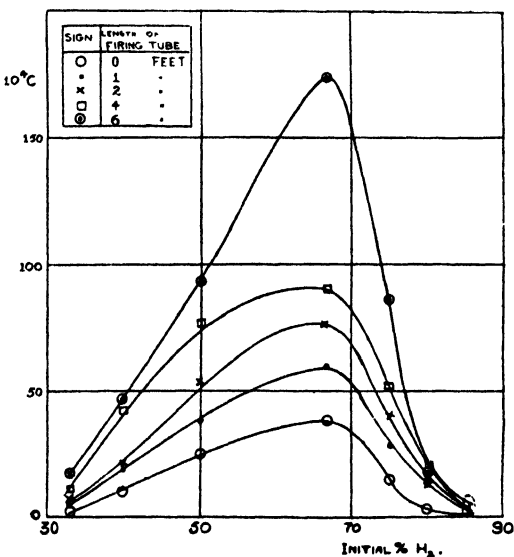
The results with hydrogen-oxygen mixtures are given in Table I. in the order in which the experiments were carried out. The values for the length of the firing tube (column 2) are given in feet, the value 0 referring to ignition close to the walls of the bomb, and the values for the maximum current which passed between the electrodes (column 3) are corrected in the same way as those given in the previous paper. The results with the mixtures  $6\text{H}_2 + \text{O}_2$  and  $4\text{H}_2 + \text{O}_2$  were always erratic, although the experiments were repeated several times.

When the values of the maximum current for a given mixture are plotted against those of the length of the firing tube,  $L$  (column 2, Table 1), the result is, within experimental error, a straight line. The equation to this is given in the fourth column of Table I., where  $d$  represents the distance between the ignition point and the centre of the electrodes. The value of  $d$  in feet is equal to  $(L + \frac{1}{4})$ . In the last column of the table is given the value of the rate of change of the current with the distance between the ignition point and the centre of the electrodes, *i.e.*,  $dC/dd$ .

From the equations in column 4, Table I., it is seen that the current passing between the electrodes increases for a given

mixture as the value of  $d$  increases. With the mixture  $6\text{H}_2 + \text{O}_2$  there is very little change in the current with  $d$  so that the exploding gas has practically the same electrical conductivity whether the explosion has travelled one foot or six feet from its source of ignition, *i.e.*, the rate of change of current with distance,  $dC/dd$ , is very small ( $+0.13$ ). This is to be expected, since the gaseous mixture is far from its detonation point. As, however, the mixture  $2\text{H}_2 + \text{O}_2$  is approached, the conductivity of the exploding gases increases very rapidly as the length of the firing tube increases, the maximum value of  $dC/dd$  being reached with this mixture. As the percentage of hydrogen in the initial gases is still further decreased beyond that demanded by the mixture  $2\text{H}_2 + \text{O}_2$ , the value of  $dC/dd$  decreases again, so that for the mixture  $\text{H}_2 + 2\text{O}_2$  it is only  $2.8 \times 10^{-4}$  amperes.

The rapid decrease in the value of  $dC/dd$  as hydrogen or oxygen is added to the mixture  $2\text{H}_2 + \text{O}_2$  is shown clearly in the figure, in which the values of the current passing between the electrodes when different firing tubes are used are plotted against the percentage of hydrogen in the initial mixture.



With the mixture containing 86 per cent. hydrogen ( $6\text{H}_2 + \text{O}_2$ ) all the values of  $C$  practically coincide; with 80 per cent. hydrogen ( $4\text{H}_2 + \text{O}_2$ ) they are distinctly separated, until with the mixture containing 67 per cent. hydrogen ( $2\text{H}_2 + \text{O}_2$ ) the effect of exploding the mixture with different firing tubes is very marked. As the amount of hydrogen decreases, this effect becomes less marked again and with 33 per cent. hydrogen ( $\text{H}_2 + 2\text{O}_2$ ), the values of  $C$  again approach each other.

These experimental results show that the current  $C$  passing between the electrodes at the centre of the spherical bomb when the gaseous mixture in it is fired by being ignited at the ends of firing tubes of different lengths screwed into its walls, can be represented by an equation of the type

$$C = C_0 + A d,$$

where  $C_0$  and  $A$  are constants and  $d$  is the distance between the firing point and the centre of the electrodes.  $C_0$ , of course, is the value of  $C$  when  $d = 0$  and is very nearly equal to the value of  $C$  when the mixture is fired at the walls of the bomb and which has been studied previously.  $C_0$ , therefore, represents the current due to the ignition of the bomb gases close to the electrodes and  $A$  represents the increase in the current due to ignition by an explosion wave which has had a run of unit length.

The rate of change of the current  $C$  with the distance  $d$ ,  $dC/dd = A$ , has a maximum value with the mixture  $2\text{H}_2 + \text{O}_2$  and decreases rapidly as hydrogen or oxygen are added. From a consideration of the results of Dixon<sup>3</sup> there is no doubt that, while the detonation wave is not set up in the mixture  $2\text{H}_2 + \text{O}_2$  when it is fired close to the walls ( $L = 0$ ), the detonation wave is certainly set up in the 6 ft. firing tube. It is uncertain whether or not the detonation wave is transmitted with unchanged velocity when it enters the bomb, but there is evidently a marked effect on the explosion, for the conductivity of the exploding gases between the electrodes is increased nearly five times. This large increase in the conductivity, however, could be caused by an increase in the maximum temperature of explosion of only  $2\text{--}300^\circ\text{C}$ . (From calculations made using the Saha equation. See Part I.<sup>1</sup>) The expulsion into the cold gases in the bomb of a considerable volume of gas from the 6 ft. firing tube, and the flame of a detonating mixture would certainly cause the gases in the bomb to be ignited over a considerable volume. This, coupled with the turbulence caused thereby would make the combustion very rapid and an increase in the temperature of explosion of  $2\text{--}300^\circ\text{C}$ . over that occurring when the gaseous mixture is fired at a point close to the walls of the bomb, might ensue. This would explain why the value of  $C$  increases with that of  $d$ , although a linear increase could not have been predicted, since both the volume of the gas expelled and the rate of its expulsion from the tube into the bomb would be increased by increasing the length of the firing tube.

*Effect of the Addition of Ethyl Iodide and Ethyl Nitrate.*—The interesting results given with the addition of different "anti-knocks" and "knock inducers" to mixtures of electrolytic gas exploded in a spherical bomb with wall ignition (Part I.) led to similar experiments being carried out with the addition of the firing tubes. Ethyl iodide was used as an example of an anti-knock and ethyl nitrate as a knock inducer. In order to introduce constant amounts of these substances into the gases in the bomb and firing tubes, one fifth of the volume of the gaseous mixture required to fill the

<sup>3</sup> *Phil. Trans.*, **200 A**, 315, 1903.

bomb and the firing tubes was saturated with the vapour of the organic liquid at room temperatures (about 19° C.), and then passed, together with the pure gases, into the bomb. The gaseous mixtures prepared in this way contained 2.8 per cent. of ethyl iodide and 2.6 per cent. of ethyl nitrate. Apart from this, there was no change in the experimental procedure.

The results of this series of experiments, expressed as before, are given in Table II.

It is uncertain whether anti-knocks and knock inducers produce their effect during the initial, or during the final or detonation stages of an explosion, or both. The results given in Table II. throw some light on this point.

TABLE II.

Mixture.	Length of Firing Tube, Feet.	10 <sup>4</sup> C. Amps.	Equation for 10 <sup>4</sup> C. Amperes.	dC/dd.
2H <sub>2</sub> + O <sub>2</sub> + 2.8 per cent. Ethyl Iodide.	0	30	22 + 11.1 d.	11.1
	2	45		
	4	60		
	6	100		
	1	36		
4H <sub>2</sub> + O <sub>2</sub> + 2.8 per cent. Ethyl Iodide.	0	1.7	0.8 + 3.4 d.	3.4
	2	6.0		
	4	22.0		
	6	21.0		
	1	3.8		
2H <sub>2</sub> + O <sub>2</sub> + 2.6 per cent. Ethyl nitrate.	0	47	40 + 26.3 d.	26.3
	2	133		
	4	183		
	6	233		
	1	73		
4H <sub>2</sub> + O <sub>2</sub> + 2.6 per cent. Ethyl nitrate.	0	5.5	3.0 + 10.1 d.	10.1
	2	40		
	4	50		
	6	60		
	1	28		

In the equation  $C = C_0 + Ad$ ,  $C_0$  represents the current when the gases are fired close to the electrodes and therefore refers to the initial stages of the setting up of an explosion wave and  $A$  gives the additional current due to unit length of firing tube and is a measure of the tendency of the mixture to detonate. If, therefore, an anti-knock or a knock inducer acts on the initial stages, it will affect  $C_0$  and if it acts on the final or detonation stages it will affect  $A$ .

The results show that, with the mixture 2H<sub>2</sub> + O<sub>2</sub> in which the detonation wave is formed in some cases, while ethyl iodide lowers and ethyl nitrate raises  $C_0$ , *i.e.*, they affect the initial stages of the explosion, only the ethyl iodide has any marked effect on the value of  $A$  or on the detonation stages, so that ethyl nitrate, which induces detonation, has very little effect when detonation is present. Similarly, with the mixture 4H<sub>2</sub> + O<sub>2</sub> which never detonates, while both ethyl iodide and ethyl nitrate affect the initial stages ( $C_0$ ), only the ethyl nitrate affects the latter stages and tends to induce detonation. Ethyl iodide, which prevents detonation, has no effect on  $A$ , *i.e.*, on the final stages, when detonation is not present.

### Summary.

It has been shown that the current  $C$  passing between electrodes placed at the centre of a spherical bomb of nearly two litres capacity, when different mixtures of hydrogen and oxygen are fired in it by ignition at the ends of firing tubes of different lengths screwed into its walls, can be represented by an equation of the type

$$C = C_0 + Ad,$$

where  $A$  and  $C_0$  are constants for any given mixture, each having a maximum value for the mixture  $2H_2 + O_2$ . The results may be explained in terms of the changes in temperature of explosion caused by the turbulence set up in the bomb by expulsion of gases from the firing tubes.

The addition of "anti-knocks" and "knock inducers" has been shown to influence the initial stages of an explosion but anti-knocks have no effect on the final stages in mixtures which do not detonate and knock inducers have no appreciable effect on the final stages of mixtures which are already detonating.

In conclusion, the author would like to express his best thanks to Dr. W. E. Garner, who suggested this research, for his very kind interest and for many valuable suggestions during the progress of the work and also to the Trustees of the Ramsay Memorial Fellowships Trust for the award of a Fellowship which has enabled this research to be carried out, and to the Department of Scientific and Industrial Research for an equipment grant.

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## INVESTIGATIONS ON GASEOUS EXPLOSIONS. PART III. IONISATION IN EXPLOSIONS OF CARBON MONOXIDE AND OXYGEN.

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The explosion of carbon monoxide with oxygen is probably the most interesting of all gaseous explosions because of the very marked influence of hydrogen and water on the ease of ignition, the rapidity of attainment of detonation and on the velocity of the detonation wave. The recent discovery by Bone<sup>1</sup> of the "activation" of nitrogen in explosions of carbon monoxide and oxygen at high initial pressures lends additional interest to the study of this explosive mixture.

The velocities of the detonation wave for the complete range of mixtures of dry and wet carbon monoxide and oxygen are not available, although a number of investigators have studied the velocities of explosion of these gases in closed vessels. Wendlandt<sup>2</sup> and Crowe and Newey<sup>3</sup> have made experiments with wet carbon monoxide-air mixtures, the former using a

<sup>1</sup> Bone, *Proc. Roy. Soc.*, 1914 to 1926.

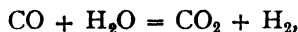
<sup>2</sup> Wendlandt, *Z. physik. Chem.*, 110, 637, 1924.

<sup>3</sup> Crowe and Newey, *Phil. Mag.* (vi), 49, 1112, 1925.

cylindrical tube at atmospheric pressure and the latter a spherical bomb at two atmospheres initial pressure. In these experiments it is shown that the greatest velocity of explosion is given by the mixture containing about 40 per cent. of carbon monoxide. This corresponds to the ratio  $\text{CO}/\text{O}_2 = 3.4$ . In order to account for this result, it is assumed that the excess of carbon monoxide over that demanded by the ratio  $\text{CO}/\text{O}_2 = 2$ , serves to suppress the dissociation of carbon dioxide and hence to raise the maximum temperature of explosion. Calculations made by the authors show that although the presence of excess of carbon monoxide suppresses the dissociation, it is not true that the temperature of explosion is raised.

The effect of water on the velocity of the detonation wave of the mixture  $2\text{CO} + \text{O}_2$  initially at atmospheric pressure, has been studied by Dixon<sup>4</sup> who found that the maximum velocity of explosion occurred when the gases contained between 5 and 6 per cent. of water. Girvan<sup>5</sup> showed that, in the presence of small traces of water, the gaseous mixture burnt very slowly, but it is only recently that a detailed study of the influence of small quantities of water has been made. Bone and Weston<sup>6</sup> have measured the quantity of electrical energy required to ignite mixtures containing varying amounts of water. This quantity was greater, the drier the mixture. When the explosion of the dry mixture does take place, it is extremely feeble and the combustion of the carbon monoxide may be far from complete. Further experiments by Bone, Newitt, and Fraser<sup>7</sup> showed that the presence of water was not essential for the explosion of carbon monoxide and oxygen; hydrogen was even better than water as a promoter of the explosion.

The earlier theories of the mechanism of the action of water in these explosions assumed that the carbon monoxide was oxidised by the water according to the equation,



the hydrogen afterwards becoming oxidised by its equivalent of oxygen and ready to repeat the cycle. Weston<sup>8</sup> and Bone, Newitt, and Fraser<sup>7</sup> from observations of the spectra of flames, believe that both the direct oxidation of carbon monoxide by oxygen and indirect oxidation by water can take place either singly or together, depending on the experimental conditions.

The electrical conductivity of exploding mixtures of carbon monoxide and oxygen has been carried out by de Muynck,<sup>9</sup> although his experiments are far from complete or conclusive. He found that the exploding mixture  $2\text{CO} + \text{O}_2$  had a greater conductivity than had either of the mixtures  $\text{CO} + 2\text{O}_2$  or  $\text{CO} + \text{O}_2$ .

### Experimental.

The apparatus employed and the experimental procedure are the same as in the case of experiments on hydrogen-oxygen mixtures,<sup>10</sup> *i.e.*, mixtures of carbon monoxide and oxygen at atmospheric pressure were exploded in a spherical bomb at the centre of which were mounted insulated circular

<sup>4</sup> Dixon, *Phil. Trans.*, **184A**, 97, 1893.

<sup>5</sup> Girvan, *J. Chem. Soc.*, **19**, 236, 1903.

<sup>6</sup> Bone and Weston, *Proc. Roy. Soc.*, **110A**, 615, 1926.

<sup>7</sup> Bone, Newitt and Fraser, *Proc. Roy. Soc.*, **110A**, 674, 1926.

<sup>8</sup> Weston, *Proc. Roy. Soc.*, **109A**, 176, 523, 1925.

<sup>9</sup> de Muynck, *Acad. Roy. de Belgique*, 1907, p. 901.

<sup>10</sup> Garner and Saunders, *Trans. Faraday Soc.*, **22**, 324, 1926.

parallel disc electrodes of platinum, one of which was surrounded by a guard ring.

A bomb of two litres capacity was used for the majority of the experiments, but a few explosions were carried out in a bomb of four litres capacity and, as far as can be ascertained, the change in the size of the bomb did not appreciably affect the results.

The great difficulty encountered in these experiments was to ensure that the gases in the bomb and the walls of the bomb possessed the same degree of dryness. After experiments with moist gases, in spite of prolonged evacuation down to 0.01 mms., several explosions with the dry gases were necessary before the conductivity gave the normal value for the dry gases. This clearly showed the marked influence of small traces of water on the ionisation produced.

In addition, if the gases were dried by a very slow passage (1 litre per hour) through long phosphorus pentoxide tubes, they could not be fired by the ignition of iron wire. With more rapid rates of streaming, e.g., 4.5 litres per hour, the gases, although normally called dry, and termed dry in this paper, contained a sufficient amount of water to enable them to be ignited. The gaseous mixtures dried in this manner gave reproducible results.

*Preparation of Gases. Carbon Monoxide.*—The carbon monoxide was prepared by the action of concentrated sulphuric acid on sodium formate. It was passed through concentrated caustic potash and soda solutions, stored over water and dried by bubbling through concentrated sulphuric acid and subsequent passage through a phosphorus pentoxide tube 1 inch internal diameter and 12 inches long.

*Oxygen.*—This was obtained by heating pure potassium permanganate. The gas was washed by passage through concentrated caustic potash solutions and dried by a phosphorus pentoxide tube similar to the above.

*Nitrogen.*—Air and cylinder oxygen were used as the source of nitrogen. They were dried by phosphorus pentoxide. No correction was made for the amount of argon present, this being recorded as nitrogen.

In addition, the gases were dried still further by passage through a phosphorus pentoxide tube placed close to the valve of the bomb.

## Results.

The results are expressed in the same way as before<sup>10</sup> and refer to explosions carried out under an initial pressure of one atmosphere at room temperatures (about 19° C.), with a potential difference, except where stated otherwise, of 2.0 volts between the electrodes. The values for the current *C* in the following tables refer to the maximum current carried by the exploding gas between the electrodes.

*Variation of Current with Voltage.*—As in the case of explosions of electrolytic gas, a linear relationship for dry mixtures of  $2\text{CO} + \text{O}_2$  was found between *C* and *V*, given by the equation  $10^\circ\text{C} = 3.1\text{V}$ , as is shown in Table I.

It thus appears that, at the temperatures of explosion, the ions are replenished as fast as they are removed by the current.

*Effect of Changes in the Composition of the Mixture.*—In the results given in Table II. the order in which the experiments are carried out is shown. The results are expressed graphically in Fig. 1 (full line) where the percentage of carbon monoxide is plotted against the initial current.

TABLE I.

Voltage Applied, V Volts.	$10^6$ C. Measured, Amperes.	$10^6$ C. Calculated, $10^6$ C. = $3 \cdot 1$ V.	Order of Expt.
1.0	4.3	3.1	5
2.0	6.1	6.2	1
4.0	12.0	12.4	2
5.0	15.5	15.5	3
6.0	18.8	18.6	4

TABLE II.

Order of Expt.	Initial Per Cent. CO.	$10^6$ C. Amperes.
3	38.6	1.41
4	53.5	3.32
5	59.9	4.31
1	66.7	6.08
6	69.9	5.79
8	72.2	4.59
7	74.6	3.95
2	78.4	3.39

From Fig. 1, it is seen that the maximum conductivity is given by the mixture  $2 \text{ CO} + \text{O}_2$ . The experimental curve is compared with the curves expected if the ionisation be chemical or of thermal origin. The dotted curve I gives that based on the assumption that the maximum current is proportional to the extent of chemical reaction at the maximum temperature of explosion and the dotted curve II is that corresponding to thermal

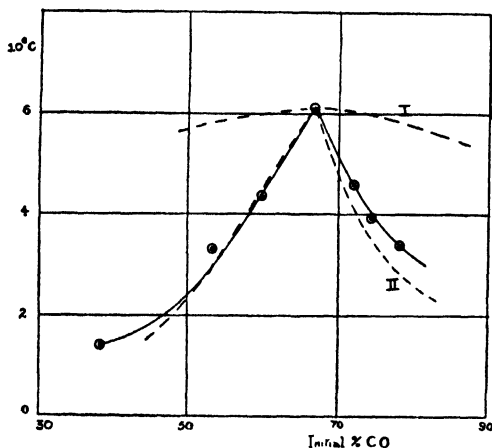


FIG. 1.

ionisation at this temperature. These calculations were made in the manner described previously,<sup>10</sup> the ionisation potential of the gases being taken as 10 volts, which is that for carbon monoxide. The results of the calculations are shown in Table III, in which the maximum temperature of explosion is given, together with the relative values of the current calculated according to the two methods.

TABLE III.

Reaction.	CO/O <sub>2</sub> Initial.	T°K.	Relative Values of Current Assuming Ionisation to be	
			Chemical.	Thermal.
$\text{CO} + \text{O}_2 = \text{CO}_2 + \frac{1}{2}\text{O}_2$	1.0	3360	29.5	$1.1 \times 10^{-6}$
$1\frac{1}{2}\text{CO} + \text{O}_2 = 1\frac{1}{2}\text{CO}_2 + \frac{1}{2}\text{O}_2$	1.5	3480	31.0	2.2 "
$2\text{CO} + \text{O}_2 = 2\text{CO}_2$	2.0	3530	31.5	2.9 "
$2\frac{1}{2}\text{CO} + \text{O}_2 = 2\text{CO}_2 + \frac{1}{2}\text{CO}$	2.5	3450	31.0	1.9 "
$3\text{CO} + \text{O}_2 = 2\text{CO}_2 + \text{CO}$	3.0	3420	30.5	1.6 "
$4\text{CO} + \text{O}_2 = 2\text{CO}_2 + 2\text{CO}$	4.0	3360	30.0	1.2 "
$5\text{CO} + \text{O}_2 = 2\text{CO}_2 + 3\text{CO}$	5.0	3240	28.0	0.6 "

(The values in the last column are the calculated values for the partial pressure of the electrons at the maximum temperature of explosion.)

From Fig. 1, it is seen that the experimental curve resembles curve II very closely. This, therefore, is further support of the view that ionisation in gaseous explosions is mainly thermal in origin.

The shape of the galvanometer curves possesses a certain interest. The records of the current passing between the electrodes during the explosion and of its variation with time are of the type shown in Fig. 2. The current

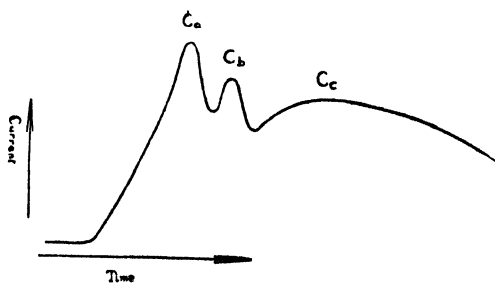


FIG. 2.

increases rapidly to a maximum value  $C_a$  and then follow two other maxima  $C_b$  and  $C_c$ , after which it falls very slowly indeed. It is the value of  $C_a$ , Fig. 2, which is recorded in all the tables in this paper. These maxima are not due to the vibrations of the galvanometer, since one complete oscillation of the fibre corresponds to only a little over  $1/10$  mm. in all these records. The maxima were separated by several mms.

As the current is still measureable some five seconds after the commencement of the ionisation, it is evident that some slow reaction is taking place even after this interval of time.

*Effect of the Addition of Nitrogen to the Dry Gases.*—These experiments were carried out in order to find whether the nitrogen acted as a diluent only, or whether there would be an increase in the ionisation due to activation of nitrogen, although Bone<sup>1</sup> does not find that nitrogen is activated in experiments with the gases at atmospheric pressure. From the results, Table IV., it appears that nitrogen acts only as a diluent. The addition of nitrogen eliminates the maximum  $C_b$ , Fig. 2.

*Comparison of the Effect of Excess of Reactants with Excess of Nitrogen.* From the results given, it is found that, when given quantities of either

carbon monoxide, oxygen or nitrogen are added to the mixture  $2\text{CO} + \text{O}_2$ , the conductivity is decreased to the same extent in each case.

TABLE IV.

Order of Expt.	Initial Per Cent. $\text{N}_2$ .	10° C. Amperes.
2 and 7	0.0	6.1
1	1.7	5.1
3	5.1	3.9
4	10.0	3.7
5	16.2	3.0
8	30.5	0.6
6	40.3	0.1

*Effect of the Addition of Water to the Dry Gases.*—As stated previously, the addition of small traces of water to the initial gases has a considerable effect on the ionisation produced during the explosion. Although many experiments were carried out on the effect of the addition of water to the initial gases, no accurate values can be given for the maximum current. The results given in Table V. refer to experiments in which the bomb walls were as dry as possible before the introduction of the wet gases; a large fraction of the water is adsorbed by the walls of the explosion vessel.

TABLE V.

Per Cent. Water in the Gases before Entering Bomb.	10° C. Amperes.
0.0	6
1.6	10
2.4	30

Not only does the value of the maximum current vary for experiments which were as far as possible identical, but the shapes of the curves given by the galvanometer vary still more. Sometimes these curves are very similar to those given by explosions of the dry gases, sometimes there is a steady maximum and sometimes they are very similar to those given by hydrogen—oxygen explosions (see Part I.). In no case, however, did the ionisation persist for as long a time as it did in the case of the dry gases.

*Effect of the Replacement of the Carbon Monoxide by Hydrogen.*—It was expected that the replacement of the carbon monoxide by small percentages of hydrogen in these explosions would increase considerably the temperature of explosion and hence the degree of ionisation produced and also that the replacement of hydrogen by small percentages of carbon monoxide would reduce the maximum temperature of explosion and the degree of ionisation in a manner very similar to that of nitrogen, since the maximum temperature of explosion of the mixture  $2\text{H}_2 + \text{O}_2$  is too high to allow of the formation of any appreciable quantity of carbon dioxide. As the percentage of carbon monoxide is increased beyond a certain value, however, the maximum temperature of explosion will be sufficiently low to allow of the formation of carbon dioxide and the gas will no longer behave as a diluent, but will burn in the wave front at the maximum temperature of explosion.

It was also expected that as the carbon monoxide of the mixture  $2\text{CO} + \text{O}_2$  was replaced by hydrogen, the characteristic galvanometer curves

for carbon monoxide-oxygen mixtures would disappear as the percentage of hydrogen was increased and give place to the curves showing the single sharp maxima of hydrogen-oxygen explosions. The experimental results which are given in Table VI. fulfilled expectations.

TABLE VI.

Order of Expt.	Per Cent. ( $2\text{H}_2 + \text{O}_2$ ).	Per Cent. ( $2\text{CO} + \text{O}_2$ ).	$10^6$ C. Amperes.
1	0.0	100.0	6.0
2	2.5	97.5	15.0
3	6.3	93.7	27.0
4	16.2	83.8	108
5	27.0	73.0	178
6	44.3	55.7	446
7	61.4	38.6	1020
8	80.1	19.9	1590
9	100.0	0.0	3820

These values for C are plotted against the initial composition of the mixture in Fig. 3, the dotted curve showing the results with the addition of nitrogen to the mixture  $2\text{H}_2 + \text{O}_2$ , for comparison.

When carbon monoxide replaces hydrogen in the mixture  $2\text{H}_2 + \text{O}_2$ , it at first acts in the same way as nitrogen, *i.e.*, as a diluent only, until about

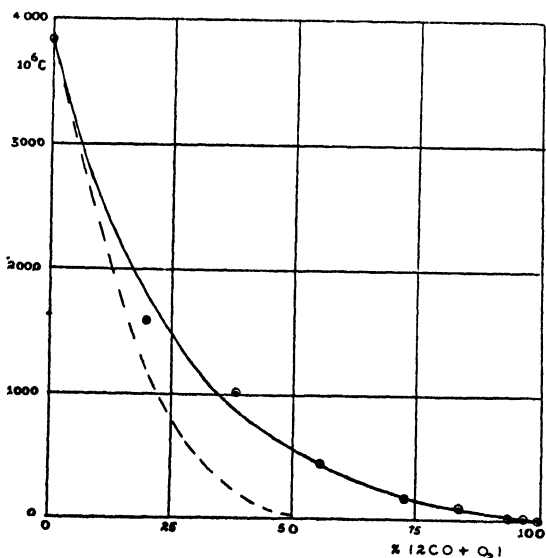


FIG. 3.

5 to 10 per cent. of the hydrogen has been replaced. With greater percentages, it begins to burn itself. This receives confirmation from experiments on the velocity of the explosion wave by Dixon and Walls,<sup>11</sup> who found that when hydrogen in the mixture  $2\text{H}_2 + \text{O}_2$  was replaced by carbon monoxide, the latter had practically the same retarding effect as an equal volume of nitrogen, until the carbon monoxide in the mixture exceeded 7.5 per cent.

<sup>11</sup> Dixon and Walls, *J. Chem. Soc.*, 123, 1025, 1923.

At the other end of the series, the mixture containing 6.3 per cent.  $2\text{H}_2 + \text{O}_2$  still gave the characteristic current/time curves for carbon monoxide-oxygen mixtures, but when the initial gases contained 16.2 per cent.  $2\text{H}_2 + \text{O}_2$ , this curve was replaced by that characteristic of hydrogen-oxygen explosions. There is a further similarity between these experiments and those of Dixon and Walls<sup>11</sup> who measured the velocity of the detonation wave in mixtures of carbon monoxide and oxygen when the carbon monoxide was gradually replaced by hydrogen, the mixture being fired by a tube containing electrolytic gas. They found that the explosion wave in the mixture  $2\text{H}_2 + \text{O}_2$  was damped down considerably as it passed into the mixture  $2\text{CO} + \text{O}_2$  and that the effect decreased as the carbon monoxide was replaced by hydrogen, until when 7.5 per cent. of the carbon monoxide had been replaced, the effect disappeared entirely and the explosion wave was continuous.

There is no doubt therefore, that there is some intimate connection between the propagation of the explosion wave and the ionisation produced.

In addition, it was found that in the experiments with 2.5 per cent. electrolytic gas, and 97.5 per cent. of  $2\text{CO} + \text{O}_2$ , the extremely long duration of ionisation, characteristic of carbon monoxide-oxygen explosions, has been decreased to about the same extent as it was in the experiments with the carbon monoxide-oxygen mixtures containing 2.4 per cent. of water vapour.

*Mechanism of the Combustion of Carbon Monoxide.*—In Fig. 2 which represents the current/time curve given by the galvanometer during the explosion of mixtures of carbon monoxide and oxygen, three maxima are shown. The first,  $C_a$ , is due to the explosion wave, and the second,  $C_b$ , is probably due to fluctuations in the temperature of the exploded gases caused by the turbulence set up by the explosion wave, since in some cases, two and even three such maxima can be distinguished. The third,  $C_c$ , must be due to some slow chemical process which takes place behind the explosion wave and which may be due to the combustion of some residual carbon monoxide, since Dixon has shown that the combustion of the carbon monoxide is incomplete in the wave front. Hydrogen and substances containing hydrogen, certainly suppress the reaction behind the wave and carbon tetrachloride (from unpublished experiments) increases it enormously. With carbon tetrachloride, not only is the duration of ionisation lengthened but also the intensity of ionisation is increased in some cases.

*Time between Firing and Measurement of Ionisation.*—As pointed out in a previous paper (Part I.), these measurements are only approximate.

Variations in the composition of the dry carbon monoxide-oxygen mixtures caused no appreciable modification in the time interval between firing and the measurement of ionisation. The replacement of carbon monoxide by hydrogen, however, resulted in this time decreasing rapidly at first and then more slowly. With no hydrogen present, this time was 0.6 seconds, but when the whole of the carbon monoxide had been replaced by hydrogen, the time decreased to 0.1 seconds. The addition of water decreased the time to about the same extent as hydrogen, namely, from 0.6 seconds with pure dry  $2\text{CO} + \text{O}_2$  to 0.2 seconds when 2.3 per cent. of water was present. As was expected, the addition of nitrogen to the mixture  $2\text{CO} + \text{O}_2$  caused the time interval to increase uniformly as the percentage of nitrogen increased; the addition of 40 per cent. nitrogen caused the time to change from 0.6 to 1.6 seconds, indicating a considerable reduction in the velocity of explosion.

*Time of Duration of Explosion.*—Unfortunately, owing to the persistence

of the ionisation, no values could be obtained for this time for mixtures of dry carbon monoxide and oxygen; the ionisation persisted in every case for over five seconds (all that could be measured), and in some cases probably for 10 or 15 seconds or more. The replacement of carbon monoxide by hydrogen, however, reduced the time rapidly at first; when 2 per cent. had been replaced, the duration of ionisation had fallen to 0.026 seconds and with pure  $2\text{H}_2 + \text{O}_2$  to 0.018 seconds. The addition of water to the mixture  $2\text{CO} + \text{O}_2$  also reduced the time of duration of ionisation to 0.3 seconds when 2.3 per cent. was present. Nitrogen also reduced the time to an extent approximately proportional to the amount added, so that with 40 per cent. nitrogen it had fallen to 0.5 second.

### Summary.

A study of the electrical conductivity of mixtures of dry carbon monoxide and oxygen exploded in a spherical bomb of two litres capacity, confirm the view that ionisation in gaseous explosions is mainly thermal in character.

The addition of hydrogen or water to dry carbon monoxide and oxygen mixtures increases the ionisation produced during the explosion. The conductivity of the gases produced during the explosion of these mixtures changes in an analogous manner to the velocity of propagation of the explosion wave.

The duration of the ionisation in the explosion of dry carbon monoxide-oxygen mixtures is much greater than for the moist gases, this being in agreement with the slow development of pressure which occurs in explosions of dry carbon monoxide and oxygen in closed vessels.

In conclusion, the authors would like to express their best thanks to Dr. W. E. Garner who suggested this research, for his kind interest and for many valuable suggestions during the progress of the work, to the Department of Scientific and Industrial Research for an equipment grant, and one of us (S.W.S.) to the Trustees of the Ramsay Memorial Fellowships Trust for the award of a Fellowship.

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## INVESTIGATIONS ON GASEOUS EXPLOSIONS. PART IV. IONISATION IN METHANE-OXYGEN AND ACETYLENE-OXYGEN EXPLOSIONS,

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These experiments were carried out in order to throw light on the mechanism of the explosive combustion of gaseous hydrocarbons, methane and acetylene being selected as examples of saturated and unsaturated compounds, and to test the accuracy of the conclusions, drawn from the results of explosions of hydrogen and oxygen and of carbon monoxide and oxygen, that ionisation in gaseous explosions is due mainly to thermal causes and does not directly result from the chemical change. In addition,

it was hoped to ascertain whether the ignition temperatures bore any relationship to the ionisation produced in the various mixtures of hydrocarbons and oxygen.

### Experimental.

The experimental procedure and the apparatus employed were exactly the same as that described previously.<sup>1</sup> Using an Einthoven string galvanometer, with a period of  $1/350$  second, measurements were made of the current passing during an explosion between two platinum circular disc electrodes, one of which was surrounded by a guard ring. The electrodes, between which a potential difference of 2.0 volts was maintained, were mounted at the centre of a spherical bomb of 1800 c.c. capacity. In this way, records were obtained of the current passing between the electrodes during the explosion and its variation with time. All the explosions were carried out at an initial pressure of one atmosphere and at room temperature, about 19° C.

*Preparation of Gases.* *Oxygen.*—Oxygen from a cylinder was used; the impurity was 5 per cent. nitrogen, for which an allowance was made. *Methane.*—A cylinder containing compressed methane was used. Analysis of the methane showed that it contained only 3.3 per cent. nitrogen as impurity. It was stored over water and dried by passage through concentrated sulphuric acid and phosphorus pentoxide. *Acetylene.*—Acetylene was prepared by the action of water on calcium carbide, the impure gas being passed through an acid solution of copper sulphate, aqueous chromic acid solution and caustic potash and then absorbed in an ammoniacal solution of cuprous chloride. After it had been well washed by decantation, the precipitated copper acetylide was decomposed by concentrated hydrochloric acid and the regenerated acetylene stored over water and dried by passage over solid potassium hydroxide and calcium chloride. In some of the later experiments, the preparation of the copper acetylide was omitted and the gas then obtained was soluble to the extent of 99.8 per cent. in a solution of ammoniacal cuprous chloride. Experiments with this gas gave results identical with those in which the purer gas regenerated from the copper acetylide was used.

### Results.

The results of the conductivity experiments are given in the same way as in the previous papers,<sup>1</sup> i.e., the value is given of the maximum current carried by the exploding gases between the electrodes between which a potential difference of two volts was maintained. These values of the current have all been corrected for small changes in the initial pressure of the explosive mixture as was done previously.<sup>1</sup>

*Change in Composition.*—The results of conductivity measurements during explosions of mixtures of methane and oxygen and of acetylene and oxygen in which the ratio of combustible gas to oxygen was varied, are given in Table I. The first column in each section gives the order in which the experiments were carried out, and in column two is given the ratio of combustible gas to that of pure oxygen obtained from pressure measurements taken during the filling of the bomb and from the analysis of the individual gases. The last column gives the value of the maximum current which passed between the electrodes during the explosion.

<sup>1</sup> Parts I., II., and III. of this series. *Trans. Faraday Soc.*, 1926-27.

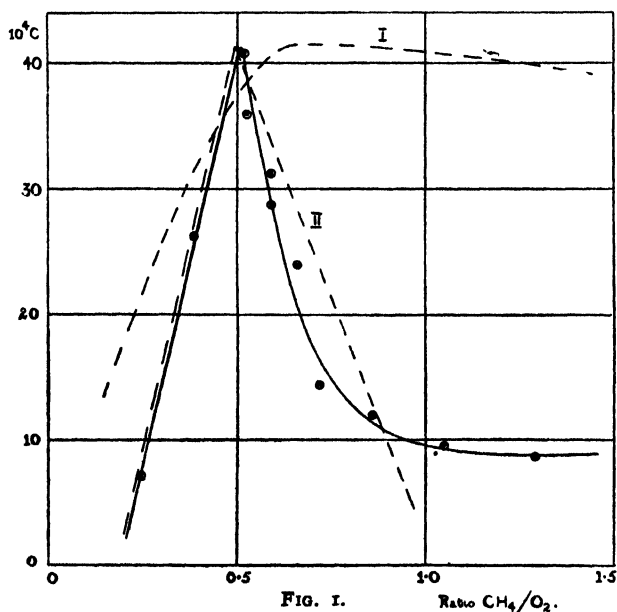
The results given in Table I. are expressed graphically in Figs. 1 and 2 in which the value of the maximum current is plotted against the ratio of methane to oxygen and acetylene to oxygen respectively in the initial

TABLE I.

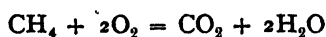
METHANE—OXYGEN MIXTURES.			ACETYLENE—OXYGEN MIXTURES.		
Order of Expt.	Ratio $\text{CH}_4/\text{O}_2$ in Initial Gases.	$10^4$ C. Amperes.	Order of Expt.	Ratio $\text{C}_2\text{H}_2/\text{O}_2$ in Initial Gases.	$10^4$ C. Amperes.
5	0.246	7.2	11	0.120	138
2	0.388	26.4	4	0.198	427
7	0.481	37.2	3	0.245	427
1	0.526	40.8	6	0.314	533
11	0.530	36.0	1	0.430	933
10	0.597	28.8	2	0.450	940
8	0.598	31.2	8	0.490	1067
12	0.658	24.0	15	0.550	1320
9	0.722	14.4	10	0.622	1707
6	0.857	12.0	13	0.655	1907
3	1.050	9.6	14	0.677	2080
4	1.290	8.6	12	0.755	1600
			9	0.845	960
			7	0.901	853
			5	0.971	693
			17	1.10	427
			16	1.20	373

The initial gases contained 4 per cent. nitrogen.

Some difficulty was experienced in firing mixtures in which the ratio of methane to oxygen was greater than unity, probably because of the relatively high ignition temperature of these mixtures.

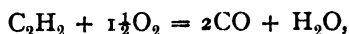
FIG. 1. Ratio  $\text{CH}_4/\text{O}_2$ .

mixture (full line). It will be noticed (Fig. 1) that the change in the ratio of methane to oxygen from 0.7 to 1.3 hardly affects the value of the current. The maximum of the curve, occurring when the ratio methane/oxygen is equal to 0.51, shows that



is the reaction which has taken place in the explosion of the mixture giving the greatest electrical conductivity.

In regard to the acetylene-oxygen mixtures, it is seen that there is a very sharp maximum when the ratio of acetylene to oxygen is equal to 0.67, which corresponds exactly to the equation,



where the current is some four times greater than that occurring with the equimolecular mixture of acetylene and oxygen, which gives the greatest velocity of detonation (Dixon).<sup>2</sup> This shows that the maximum conductivity of the exploding gases occurs for the mixture in which the hydrogen is burnt

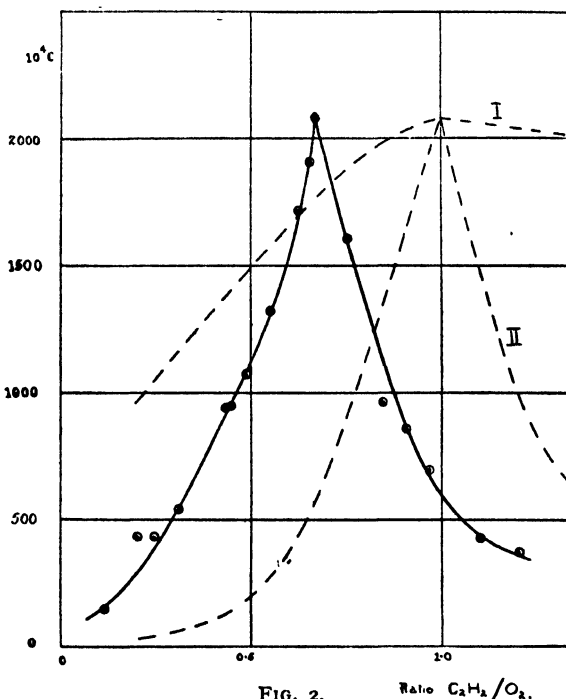


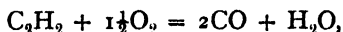
FIG. 2. Ratio  $\text{C}_2\text{H}_2/\text{O}_2$ .

to water and the carbon to carbon monoxide, a result which is different from that obtained with methane-oxygen mixtures, where the maximum occurred when the carbon was burned to carbon dioxide. These results, however, although they appear conflicting are quite compatible with one another.

It is well known that, owing to the endothermic character of acetylene, the explosion temperatures of acetylene-oxygen mixtures are much higher than those of methane-oxygen mixtures (see p. 262), and that at the maximum temperature of explosion, the carbon dioxide produced is considerably dissociated into carbon monoxide and oxygen. There is every reason to believe, therefore, that with acetylene-oxygen explosions, the carbon dioxide will be dissociated to a greater extent than it will in the case of methane-oxygen explosions and from theoretical calculations, it can be

<sup>2</sup> Dixon, *Phil. Trans.*, 184 A, 97, 1893; 200 A, 315, 1903.

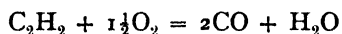
shown that the maximum temperature attained with the former mixtures is so high that practically no carbon dioxide can exist, and that any oxygen added beyond the amount demanded by the equation,



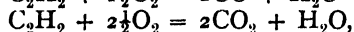
acts as a diluent. Hence, if ionisation be a thermal effect, the maximum conductivity will occur when the carbon is burnt to carbon monoxide.

Some discrepancy occurs, however, with regard to the water formed, for according to the conductivity experiments, the hydrogen is burnt to water in the mixture giving the greatest conductivity, whereas according to the theoretical calculations, the water should also be dissociated to a considerable extent, and the maximum temperature should occur when the ratio of acetylene to oxygen is equal to unity (see p. 262). The theoretical calculations cannot be very exact, however, at such high temperatures, and the calculated temperature may not be reached on account of heat losses. It is very probable, therefore, that the ionisation experiments, give a true indication of the temperatures reached and that for acetylene-oxygen mixtures, the maximum temperature is reached when the hydrogen is burnt to water.

If, however, the temperature of explosion is reduced by addition to the initial mixture of considerable quantities of nitrogen, the carbon dioxide will not be dissociated to such a great extent at the maximum temperature of explosion and hence oxygen added beyond the amount required by the above equation will not act as a diluent but will enable the combustion of the carbon monoxide to proceed. Hence the maximum temperature of explosion will occur when the amount of oxygen in the initial mixture is between that demanded by the equations,



and



*i.e.*, when the ratio of acetylene to oxygen is between 0.67 and 0.40, the actual value depending on the amount of nitrogen added. Thus the addition of a constant amount of nitrogen to acetylene-oxygen mixtures should reduce the current carried by the exploding gases and shift the position of the maximum of the current-composition curve towards the oxygen side. That it does so is shown by the following series of experiments.

#### **Effect of the Addition of 70 per cent. Nitrogen to Acetylene-Oxygen Mixtures.**

In these experiments, the nitrogen was obtained from the air, the required ratio of nitrogen to oxygen being obtained by the use of air and cylinder oxygen. No account is taken of the argon present, which is included as nitrogen. The results, expressed as before, are given in Table II. and are expressed graphically in Fig. 3 (full line).

Fig. 3 shows that, although the addition of nitrogen has not greatly changed the shape of the curve, the maximum has shifted considerably and occurs when the ratio of acetylene to oxygen is equal to 0.54, showing that carbon dioxide is produced to a large extent in the explosion of the mixture which gives the greatest electrical conductivity.

It is interesting to compare the experimental curves with curves calculated on the assumption that ionisation is due to (a) the chemical reaction and (b) a thermal process as in the case of hydrogen-oxygen and

carbon monoxide-oxygen mixtures.<sup>1</sup> In order to make these calculations, it is necessary to evaluate the maximum temperature of explosion; as the calculations were very laborious, only a few were made. The data employed

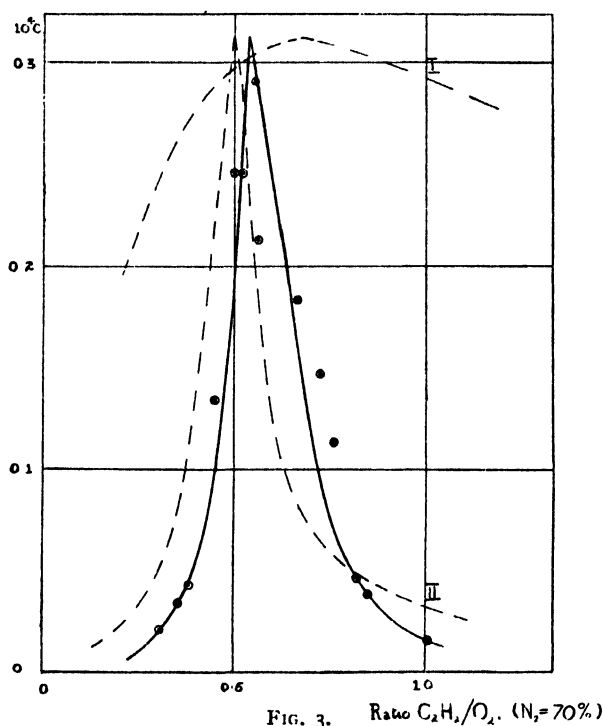
TABLE II.

Order of Expt.	Ratio $C_2H_2/O_2$ in Initial Gases.	$10^4$ C. Amperes.	Order of Expt.	Ratio $C_2H_2/O_2$ in Initial Gases.	$10^4$ C. Amperes.
4	0.301	0.0210	7	0.579	0.2114
3	0.345	0.0494	12	0.662	0.1838
5	0.377	0.0558	8	0.688	0.1480
1	0.453	0.1334	9	0.764	0.1136
2	0.497	0.2471	14	0.815	0.0460
6	0.523	0.2470	13	0.846	0.0390
11	0.552	0.2918	10	1.002	0.0152

The initial gases contained 70.0 per cent. nitrogen.

have been given elsewhere.<sup>3</sup> The values thus obtained for the maximum temperatures of explosion are given in the third column of Table III.

The extent to which chemical reaction takes place at the maximum temperature of explosion has been calculated from the number of molecules

FIG. 3. Ratio  $C_2H_2/O_2$ . ( $N_2=70\%$ )

of methane or acetylene decomposed and the number of molecules of carbon monoxide, carbon dioxide and water formed. It has been assumed that each reaction, whether the decomposition of a methane or acetylene molecule or the formation of a molecule of carbon monoxide, carbon dioxide or water, gives rise to the same number of electrons. The values

<sup>3</sup> Saunders, *J. physical Chem.*, **28**, 1151, 1924.

given in the fourth column of Table III. are based on a hundred molecules of the initial mixture and are relative only.

The partial pressure of the electrons at the maximum temperature of explosion has also been calculated using the Saha equation.<sup>4</sup> Here again, because of the uncertainty of the values of the ionisation potentials of the various gases present, no accurate calculation can be made, but, taking an ionisation potential of 10 volts for each gas, approximately relative values of the partial pressure of the electrons can be calculated, since the products of each explosion contain the same gases. The values thus calculated are given in the fifth column of Table III.

TABLE III.

Reaction.	Ratio.	$T_m^{\circ}$ K.	Relative Values of Current Assuming Ionisation to be	
			Chemical.	Thermal.
<i>Methane and Oxygen :—</i>				
$\text{CH}_4 + \frac{1}{2}\text{O}_2 = \text{CO} + 2\text{H}_2$	2'00	800	133	Negligible
$\text{CH}_4 + \text{O}_2 = \text{CO} + \text{H}_2\text{O} + \text{H}_2$	1'00	3140	150	$0.42 \times 10^{-6}$ atm.
$\text{CH}_4 + 1\frac{1}{2}\text{O}_2 = \text{CO} + 2\text{H}_2\text{O}$	0'67	3770	152	11.8 " "
$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$	0'50	3840	128	16.6 " "
$\text{CH}_4 + 3\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} + \text{O}_2$	0'33	3680	105	6.6 " "
$\text{CH}_4 + 5\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} + 3\text{O}_2$	0'20	3440	58	2.0 " "
<i>Acetylene and Oxygen :—</i>				
$2\text{C}_2\text{H}_2 + \text{O}_2 = 2\text{CO} + 2\text{C} + 2\text{H}_2$	2'00	3790	133	13.9 " "
$\text{C}_2\text{H}_2 + \text{O}_2 = 2\text{CO} + \text{H}_2$	1'00	5200	150	1300.0 " "
$\text{C}_2\text{H}_2 + 1\frac{1}{2}\text{O}_2 = 2\text{CO} + \text{H}_2\text{O}$	0'67	4650	120	354 " "
$\text{C}_2\text{H}_2 + 2\text{O}_2 = \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$	0'50	4320	108	116 " "
$\text{C}_2\text{H}_2 + 2\frac{1}{2}\text{O}_2 = 2\text{CO}_2 + \text{H}_2\text{O}$	0'40	4220	96	79.4 " "
$\text{C}_2\text{H}_2 + 4\text{O}_2 = 2\text{CO}_2 + \text{H}_2\text{O} + 1\frac{1}{2}\text{O}_2$	0'25	3960	76	27.5 " "
<i>Acetylene, Oxygen and 70 % Nitrogen :—</i>				
$2\text{C}_2\text{H}_2 + \text{O}_2 = 2\text{CO} + 2\text{C} + 2\text{H}_2$	2'0	2420	133	1.0 $10^{-8}$ " "
$\text{C}_2\text{H}_2 + \text{O}_2 = 2\text{CO} + \text{H}_2$	1'0	2590	150	7.1 " "
$\text{C}_2\text{H}_2 + 1\frac{1}{2}\text{O}_2 = 2\text{CO} + \text{H}_2\text{O}$	0'67	3090	160	26.5 " "
$\text{C}_2\text{H}_2 + 2\text{O}_2 = \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$	0'50	3330	156	101 " "
$\text{C}_2\text{H}_2 + 2\frac{1}{2}\text{O}_2 = 2\text{CO}_2 + \text{H}_2\text{O}$	0'40	3230	130	94.6 " "
$\text{C}_2\text{H}_2 + 4\text{O}_2 = 2\text{CO}_2 + \text{H}_2\text{O} + 1\frac{1}{2}\text{O}_2$	0'25	2960	120	11.1 " "

These calculated values are compared with the experimental results in Figs. 1, 2, and 3 where the full line is the experimental curve and the dotted lines represent the current assuming the ionisation to be proportional to the extent to which chemical action takes place (Curve I.) and to be a thermal effect (Curve II.). The latter curves are relative, having been reduced to a basis such that the maximum of each coincides with that of the experimental curve.

From a consideration of these curves, it is seen that with methane-oxygen mixtures and acetylene-oxygen mixtures containing 70 per cent. nitrogen, the thermal ionisation curve (Curve II.) fits the experimental results very closely, whereas not only is the chemical ionisation curve (Curve I.) much too flat, but its maximum is in the wrong position.

With acetylene-oxygen mixtures alone, although the thermal ionisation curve (Curve II., Fig. 2) is of the right shape, its maximum, together with

<sup>4</sup> Saha, *Phil. Mag.* (vi.), 40, 72, 1920.

that of the chemical ionisation curve (Curve I.) occurs when the ratio of acetylene to oxygen is equal to 1.0, whereas the maximum of the experimental curve occurs when this ratio is 0.67. This discrepancy has already been discussed.

Although these considerations are of a qualitative nature, they confirm the conclusion reached from a study of the ionisation produced during the explosion of hydrogen-oxygen and carbon monoxide-oxygen mixtures, that ionisation in gaseous explosions is very largely thermal in character.

#### Effect of the Addition of Nitrogen with the Ratio of the Combustible Gas to Oxygen Constant.

The results with the addition of varying quantities of nitrogen to mixtures of methane and oxygen and acetylene and oxygen, in which the ratio of combustible gas to oxygen was kept at a constant value of 0.60 and 0.67 respectively, are given in Table IV. and expressed graphically in Figs. 4 and 5.

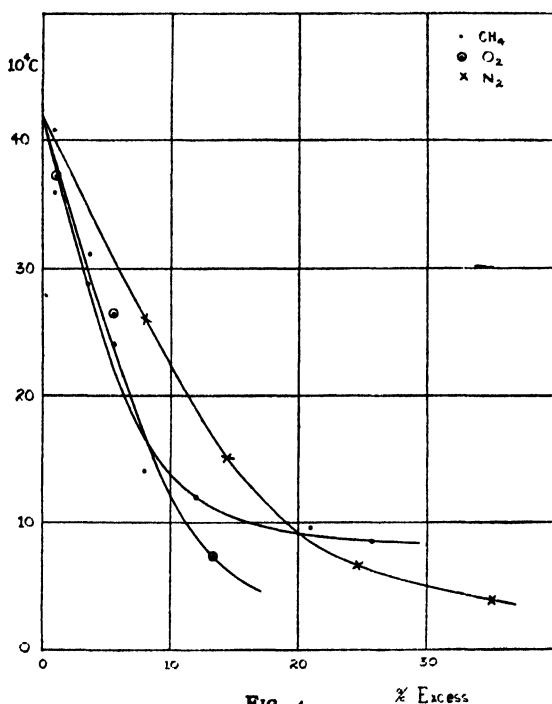


FIG. 4.

In the case of mixtures of methane and oxygen, those which contained more than 40 per cent. nitrogen could not be exploded under the experimental conditions. From Table IV. and Fig. 4 it is seen that the conductivity decreases as the percentage of nitrogen in the initial mixture increases, an expected result, since the addition of nitrogen lowers the maximum temperature of explosion and also decreases the concentration of the reacting gases. With acetylene-oxygen mixtures, the results, Table IV. and Fig. 5, are a consequence of two effects, a diluent effect and a shift in the maximum of the current/composition curve, but they do not differ greatly from the effect of nitrogen on the other explosions studied.

*Time between Firing and the Measurement of Ionisation.*—Owing to the method of measurement, these times are approximate and relative only.

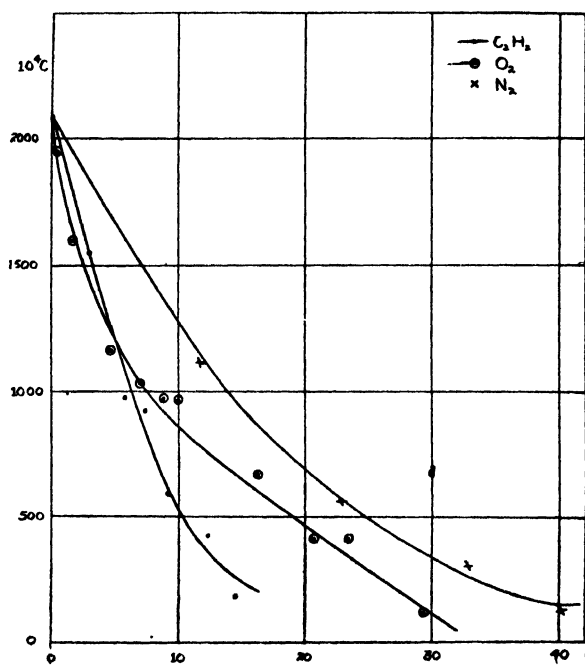


FIG. 5. % Excess.

No great change in the time elapsing between the moment the current was passed through the firing plug and the measurement of ionisation was found with mixtures of methane and oxygen, the average time interval being 0.60 seconds, but with the addition of nitrogen to the mixture in which the

TABLE IV.

Order of Expt.	Per Cent. $\text{N}_2$ Initially.	$10^4$ C. Amperes.
Ratio of methane to oxygen in initial gases = 0.60.		
—	4.0	30
1	12.0	18.6
2	18.8	10.7
3	28.6	4.7
4	39.1	2.7
Ratio of acetylene to oxygen in the initial gases = 0.67.		
1	3.0	2100
2	11.7	1113
3	22.8	552
4	32.6	320
5	40.1	128
6	70.0	0.154

ratio of methane to oxygen was 0.60 this time was progressively increased to nearly 3 seconds with 40 % nitrogen, showing that the rate of explosion had decreased considerably.

This time interval did not vary within experimental error for any of the mixtures of acetylene and oxygen, the mean value being 0.48 seconds, nor

did it vary with the ratio of acetylene to oxygen in the experiments in which 70 % of nitrogen was present, the mean value in these experiments being 0.59 seconds.

*Time of Duration of Ionisation.*—These values of the time of duration of the ionisation which could be measured are relative only, since the measurement of this time interval will be dependent on the sensitivity of the galvanometer.

With methane-oxygen mixtures, the ionisation could be measured for 0.045 seconds with the mixture in which the ratio of methane to oxygen was 0.246, but decreased steadily to a minimum value of 0.018 seconds. When this ratio was 0.722 and then uniformly increased to 0.040 seconds as the ratio was increased to 1.29. Addition of nitrogen to the mixture in which the ratio methane/oxygen was 0.60 did not appreciably change the time of duration of ionisation.

The time the measurable ionisation persisted did not appreciably change for any of the explosions of acetylene-oxygen mixtures, the mean value being 0.015 second. This time was increased considerably, however, by the addition of nitrogen, although the values became very erratic, as the ratio of acetylene to oxygen was varied. For the experiments in which 70 % of nitrogen was present, the mean value of the time of duration of ionisation was 0.132 second.

### Comparison of the Effect of Excess of Reactants with Excess of Nitrogen.

As in the case of explosions of hydrogen and oxygen<sup>1</sup> it is interesting to compare the effect of the addition of either of the reacting gases, oxygen, methane and acetylene, beyond the amount demanded by the mixture giving the greatest conductivity, with the effect of the addition of nitrogen. These comparisons are shown graphically in Figs. 4 and 5 for mixtures containing methane and acetylene respectively. In the case of mixtures containing methane, the maximum current for methane-oxygen explosions was found when the ratio of methane to oxygen was equal to 0.51, but nitrogen was added to the mixture in which this ratio was 0.60. As however, the current increases from 30 to  $42 \times 10^{-4}$  amperes with a decrease in the methane/oxygen ratio from 0.60 to 0.51, the figures obtained for the experiments on the addition of nitrogen have all been multiplied by the value 42/30 so as to enable a comparison with the reacting gases to be made (Fig. 4).

If Figs. 4 and 5 are compared with the corresponding curves for hydrogen and oxygen explosions,<sup>1</sup> no similarity is observed; sometimes the nitrogen curve is above the oxygen curve and sometimes below, and the same occurs with the other gases. Why this should be so is not apparent and no explanation can be given at present. It is interesting to note, however, that with hydrogen-oxygen-nitrogen explosions, the nitrogen curve is the lowest, whereas with methane and acetylene mixtures, it is the highest, *i.e.*, the addition of nitrogen causes the exploding gas to carry a greater current than does the addition of either reactant.

*Ignition Temperature and Ionisation.*—Although there appeared to be a connection between the ignition temperature and the ionisation during the explosion of mixtures of hydrogen and oxygen,<sup>1</sup> the results are not confirmed by the methane-oxygen and acetylene-oxygen experiments, for excess of methane beyond that required for complete combustion raises the ignition temperature but has practically no effect on the conductivity

up to 10 per cent. excess and beyond this amount it increases the conductivity, whereas the opposite effect should take place if the ignition temperature bore any relationship to the ionisation. In the case of acetylene-oxygen mixtures, excess of acetylene probably lowers the ignition temperature and therefore should increase the conductivity; the reverse effect is found, however, and the conductivity decreases. It thus appears that there is no connection between ignition temperatures and ionisation during the explosion of these gaseous mixtures.

### Summary.

From a study of the ionisation during the explosion of mixtures of methane and oxygen and of acetylene and oxygen, it has been shown that the maximum electrical conductivity occurs when the hydrogen is burnt to water and the carbon to carbon dioxide in the case of the former mixtures and when the hydrogen is burnt to water and the carbon to carbon monoxide in the latter. The addition of 70 per cent. of nitrogen to the acetylene-oxygen mixtures lowers the maximum temperature of explosion sufficiently for combustion of carbon monoxide to carbon dioxide to occur in the mixtures giving the greatest electrical conductivity. The conclusion previously reached, that the ionisation is a thermal and not a chemical effect has been confirmed, and it has been shown that there is probably no connection between ionisation during explosion and the ignition temperature of the initial gaseous mixture.

In conclusion, the author would like to express his best thanks to Dr. W. E. Garner who suggested this research for his kind interest and for many valuable suggestions during its progress, to the Trustees of the Ramsay Memorial Fellowships Trust for the award of a Fellowship which has enabled the work to be carried out, and to the Department of Scientific and Industrial Research for an equipment grant.

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### REVIEWS OF BOOKS.

**Stainless Iron and Steel.** By J. H. G. MONYPENNY, F.INST.P. (London, 1926: Chapman & Hall Ltd. Pp. ix + 304 with 22 plates. Price 21s.)

The remarkable development of stainless steels since their introduction by Brearley in 1913 is an indication of the demand for engineering materials possessing the range of strength and ductility obtainable only in steel, combined with a greatly increased resistance to corrosion and oxidation. The annual cost to the world of the corrodibility of steel amounts to figures which at first sight seem fantastically high. It is only the relatively high first cost of the stainless steels which stands in the way of a far more rapid increase in their use.

The author, by his wide experience in the study and manufacture of stainless steels, in association with Brearley, was exceptionally well qualified to write the first comprehensive book on the subject and has discharged his task with conspicuous success. The point of view is practical but the author's treatment is thoroughly scientific wherever possible; it must be admitted that much of our knowledge of the stainless steels is still empirical. The book is packed with

information and quantitative data, on nearly all aspects of the subject, gained in the laboratory and steel works with which the author is associated or in the works of other manufacturers. It is specially strong on the metallographical side. The relation of properties to structure and the effect on both of these of heat-treatment and the position and character of the thermal critical points are held in view throughout.

All the stainless steels owe their resistance to corrosion to their chromium content in the first place and it is only in the newer "austenitic" varieties that the presence of other alloy elements, nickel in particular, is necessary to secure the special type of non-corrodibility required. The stainless steels used for cutlery and for many engineering purposes differ little from the composition first developed by Brearley, with about 13 per cent. chromium and 0.3 per cent. carbon, while "stainless iron," otherwise similar in composition but with about 0.1 per cent. of carbon, has its own field of application owing to its greater ductility and its capacity for being cold-worked without losing resistance to corrosion. A knowledge of the iron-chromium-carbon series of alloys is therefore of primary importance, though the effect of additions of nickel, molybdenum, etc., and of variation in silicon, manganese and sulphur content may be large. The consideration of the relative corrodibility of different stainless steels and the observation that no variety resists all types of corrosive attack may obscure the fact that the corrodibility of steel is enormously diminished by a chromium content exceeding 12 per cent., to such an extent indeed that it becomes practically incorrodible in the conditions of many kinds of actual service.

An interesting historical sketch is followed by chapters on the influence of chromium on the structure and hardness of steel, the manufacture and treatment of stainless steel, mechanical and physical properties, influence of varying treatment and composition on resistance to corrosion, resistance to different corroding media, "special" stainless steels, and applications of stainless steels.

The significance of the low carbon content, about 0.3 per cent., of the eutectoid (pearlite) and the importance of carbon content generally in stainless steels are fittingly stressed by the author. In general, resistance to corrosion increases with increasing chromium and diminishing carbon content; the limitation of the operation of these factors by other considerations is clearly explained. The treatment and mechanical properties of the stainless steels are largely influenced by the effect of chromium in raising the temperature of the  $A_c$  and  $A_r$  critical points and retarding the separation of ferrite and carbide during cooling, and by the accentuation of the latter effect when the initial temperature is raised. The development of steels specially resistant to particular forms of corrosion and the wide range of mechanical properties, controlled by variation of composition and treatment, now give a choice of stainless steels comparable in variety with all the other alloy steels taken together. Among the useful purposes served by Mr. Monypenny's book are the restoration of order in this seeming confusion, and guidance in the selection of suitable types of stainless steel according to the purpose in view.

The author makes some interesting observations on the patent position, and due credit is given to Strauss and Maurer for their independent development of austenitic stainless steels. The book is written in a clear and direct style and is very readable. On some points the explanations given are perhaps longer than is necessary for the scientific metallurgist, but these are probably well worth while in view of the wide circle of readers to whom the book will appeal. The use of "Brinell" as a verb (p. 124 "they were quenched out in water and

subsequently Brinelled") is more appropriate to the workshop than to a scientific treatise.

The abundant illustrations do justice to the well-known skill of the author in photomicrography and the printing and production of the book are excellent. In this respect indeed, the publishers have gone to extremes. The book is not a large one if judged by its contents, yet it weighs  $2\frac{1}{2}$  lbs. Of the 304 numbered pages 14 are completely blank and 10 contain only the title of a chapter which appears again in its proper place. A stout, heavily loaded paper is necessary for the photomicrographs but not for the rest of the contents. A book of this weight is physically burdensome to read if held in the hand. The value of its contents is such as to render quite unnecessary any attempt to make the book appear more substantial than it really is.

It is probably safe to assume that every maker of stainless steel already has Mr. Monypenny's book. All who are interested in the use or study of any of the many varieties of this increasingly important material cannot do better than make themselves well acquainted with the book.

H. M.

**Wireless Pictures and Television.** By T. THORNE BAKER. (London: Constable & Co. Ltd. Pp. 88, x. Price 6s. 6d. net.)

The author is an enthusiast in his subject and his survey of the progress which has so far been made in the telegraphy of pictures reflects his keen interest. He has, however, found difficulty in deciding as to what type of reader he is addressing. Modern developments in wireless telephony have led to the growth of a large class of "amateurs" with very limited scientific knowledge. The book appears to be addressed mainly to this class; much matter of an elementary nature is introduced in order to make the story intelligible to such readers, who, nevertheless, are unlikely to appreciate the occasional mathematical treatment. Perhaps the most striking instance, of the manner in which the author thus falls between two stools, occurs in Chapter III., where, after the author feels it necessary to explain the nature of a galvanometer, he proceeds in the next few pages to discuss the Einthoven galvanometer and the cathode ray oscillograph.

The ample references to original papers, however, render the book useful to the more serious worker. It is well written and free from serious printers' errors. The illustrations are admirably reproduced.

**Report of the Committee of the Privy Council for Scientific and Industrial Research, for the year 1925-1926.** (London, H.M.S.O.; Paper wpr. Pp. iv + 178. 3s. net.)

This publication gives, *inter alia*, the report of the Advisory Council and a summary of the work of the Research Organisations of the Department, and deals with developments in the organisation of research in other parts of the Empire.

**The Development and Present Position of Chemical Analysis by Emission Spectra.** By F. TWYMAN. (London: Adam Hilger, Ltd. Pp. 43. 2s. 6d. net.)

The booklet comprises two lectures delivered before the Sheffield Metallurgical Association in December, 1924.

# THE ACTION OF IRON AS AN IMPURITY IN THE LEAD ACCUMULATOR.

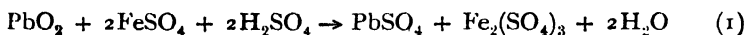
BY FREDERICK MEASHAM LEA AND JOHN TEARE CRENNELL.

(Received 28th March and read before THE FARADAY SOCIETY,  
25th May, 1927.)

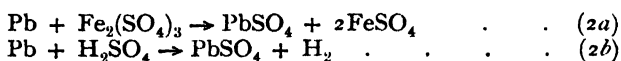
## PART I. CAPACITY LOSS DUE TO SELF-DISCHARGE.

Iron has generally been considered as a serious impurity in the lead accumulator, but until recently little definite evidence of its action has been forthcoming.

Dolezalek<sup>1</sup> has proposed the theory that metals capable of existing in more than one valency stage in the electrolyte, and lying above lead in the electromotive series, cause a loss of capacity in a cell by undergoing repeated cycles of oxidation at the positive plate and of reduction at the negative plate. Parr<sup>2</sup> and Vicarey<sup>3</sup> stated that iron has serious effects on the lead accumulator, but advanced little definite evidence regarding the nature of its action. Gillette<sup>4</sup> carried out "poisoning" experiments on lead cells with various impurities, including iron, but did not examine the actions occurring. Vinal and Altrup<sup>5</sup> studied the effect of iron on the rates of sulphation of positive and negative plates by a weighing method. The increase in weight of a positive plate immersed in a sulphuric acid solution containing ferrous iron, as compared with a similar plate in a pure acid, was found to be in agreement with that required by the equation,



this being the normal self-discharge equation for the positive plate according to the Dolezalek theory. The introduction of a negative plate into a solution containing a positive plate which had come to equilibrium with its solution, *i.e.* when equation (1) was complete, was found to lead to a further increase in the positive plate weight, showing that equation (1) was recommencing owing to the reduction of ferric to ferrous iron at the negative plate and its re-oxidation, according to equation (1), at the positive plate. The action at the negative plate was represented by the two equations,



The weight increases for a negative plate immersed in a sulphuric acid solution of ferric sulphate, compared with a plate in pure acid, were found

<sup>1</sup> "The Theory of the Lead Accumulator." (Trans. by Von Ende, 1904.)

<sup>2</sup> *J. Inst. Elec. Eng.*, 36, 406 (1905-06).

<sup>3</sup> *Trans. Faraday Soc.*, 2, 222. <sup>4</sup> *Trans. Amer. Electrochem. Soc.*, 41, 217 (1922).

<sup>5</sup> *J. Amer. Inst. Elec. Eng.*, 1924, 313.

to be in excess of the amount calculated by equation (2a). This was interpreted by Vinal and Altrup as indicating that the presence of iron accelerates the action (2b), but this accelerating action was found to be greatest in the initial stages and to die out after equation (2a) had come to equilibrium (about 150 hours). It was calculated that the velocity of the reaction (2b) had been increased, during the pre-equilibrium period, about 7 and 3 times for solutions containing 0.08 per cent. and 0.012 per cent. iron respectively. These actual figures appear to be due to an error in calculation, the correct values, from the data given, being 3.77 and 1.35. This acceleration of reaction (2b) has not been confirmed in the present investigation. The results of these workers constitute proof of the accuracy of the Dolezalek theory, but do not give any quantitative data concerning the actual rates of capacity loss in a complete cell.

### General Outline of the Investigation.

The method employed in this work has been the "poisoning" of cells by introducing known amounts of iron into the electrolyte. Experiments of a semi-quantitative nature were carried out initially at laboratory temperatures by selecting groups of four cells of equal capacity, as determined by a long series of preliminary cycles of charge and discharge, and introducing iron into the cells so that in any one group the iron concentrations in the electrolyte were 0.1, 0.01, 0.001 and zero, gms. of iron per 100 c.c. (In actual practice the "zero" cell always contained some iron derived from the cell materials which was not completely removable by changing the electrolyte.) Such groups exhibited two types of capacity loss proportional to the iron concentration in a cell.

(a) A cell containing iron when discharged after various periods of standing was found, compared with a cell with pure electrolyte, to show a loss of capacity increasing with time. This loss is termed the "Self-discharge" loss and is due to the action of the iron as suggested by the Dolezalek theory.

(b) A cell containing iron, if discharged immediately after charge, exhibited a loss of capacity compared with a cell containing pure electrolyte. This loss is termed the "Permanent" loss as it has been shown that it cannot be due to self-discharge similar to (a) during the period required for discharge.

Similar groups of cells were permitted to stand in a discharged condition for periods up to 36 days, to determine if iron had any effect on the so-called "sulphation" produced in a lead cell when standing discharged. These cells were then charged and immediately discharged. A loss of capacity of type (b) was observed in cells containing iron, equal in magnitude to that observed in the previous experiments, but otherwise these cells gave their normal capacities, showing that such "sulphation" was neither influenced by the presence of iron nor actually occurring. In order to determine that no other effects beyond (a) and (b) were occurring, two groups, each of four cells (One type A, one type B as described later) were charged and discharged on alternate days at the normal rates (5 to 7 hour rates). Two further groups (One type A, one type B) were discharged at the one hour rate and recharged at the normal rate on the same day. In neither case was any effect on the life of the cells observed. The cells discharged at the one hour rate all showed marked loss of capacity, due to loss of positive paste, after nearly 200 cycles, but no relation between the iron content and this loss was found, while after about 75

cycles those discharged at the normal rate showed no deterioration for any iron content.

A close check was kept on the electrolyte iron concentrations of all cells. It was found that the iron tends to become unequally distributed throughout the electrolyte of a cell, the concentration increasing towards the bottom. In addition the iron is adsorbed by the positive paste (lead-peroxide), and the resulting equilibrium is dependent on a number of factors. This adsorption has been found to be related to the Permanent loss occurring in a cell containing iron, and for convenience the discussion of these effects has been deferred to the second paper.

### Experimental Procedure.

*Types of Cells.*—Two types of cells have been used, details of which are shown in the adjoining Table.

*Iron Content of Plates and Electrolyte.*—Analyses showed that the iron introduced into the cell by the plates was 0.085 g. per cell for type A and 0.057 g. for type B. In both cases the positive plates contained the greater percentage of the iron impurity. The electrolyte of the cells was changed until the electrolyte iron concentration was less than 0.0006 g./100 c.c. for type A and less than 0.00025 g./100 c.c. for type B, and these are the iron concentrations of cells referred to as pure, unless otherwise stated. It was impossible to eliminate the iron completely from a cell owing to its adsorption by the lead peroxide.

Cells were made up to a given electrolyte iron concentration by the addition of pure ferrous sulphate dissolved in 1.220 S.G. sulphuric acid. All iron and acid removed

Type of Cell.	Type and Number of:—		Dimensions of Plates. (Cms.)			Weight of Paste. (g.)		Distance between Plates. Cm.	Volume of Electrolyte. C.c.	Capacity at 3 Amperes to 1.83 Volts. A.H.	Remarks.
	Positive Plates.	Negative Plates.	Height.	Width.	Thickness.	Positive.	Negative.				
A	Pasted 2	Pasted 3	10.2 <sup>6</sup> 10.2 <sup>7</sup> 10.2 <sup>8</sup>	9.75 9.75 9.75	0.49 0.32 0.49	300	350	0.5	750	17	Wood separators. Glass containers. 1.5 cm. space below plates.
B	Semi-Plante 1	Pasted 2	18.9 <sup>6</sup> 18.9 <sup>7</sup>	13.4 13.9	0.6 0.5	350	800	0.6	2000	20	Wood separators. Glass containers. 3.5 cm. space below plates.

<sup>6</sup> Positive plates.

<sup>7</sup> Outside negative plates.

<sup>8</sup> Middle negative plate.

<sup>9</sup> Negative plates.

from cells for analyses was replaced at intervals, so maintaining the total acid and iron contents of a cell constant. Cells in any group were worked in series and subjected to the same treatment.

*Estimation of Iron.*—The estimation of iron present in small concentrations in sulphuric acid solution was carried out by titration with titanous chloride, using methylene blue as indicator. A titanous chloride solution of approximate strength 1 c.c. = 0.0001 g. iron was employed together with an apparatus as described by Knecht and Hibbert.<sup>10</sup> The sulphuric acid-iron solution to be estimated was oxidised with  $N/250$  potassium permanganate, boiled with 5 c.c. hydrochloric acid (1 part concentrated acid : 3 parts water) to destroy excess permanganate, diluted with distilled water so that the volume of solution at the end of the titration was about 25 c.c., and 1 c.c. of a methylene blue solution of known titre added (usually about 0.4 c.c. of the standard titanous chloride solution). Titrations were carried out with a nearly boiling solution in a carbon dioxide atmosphere, using flasks which were closed except for a gas escape hole. At lower temperatures the velocity of reduction of methylene blue by the weak titanous chloride solution is slow, leading to poor end-points. It was found necessary to work with constant hydrochloric acid content and volume of solution, as the titre of the methylene blue indicator was somewhat dependent on the hydrochloric acid concentration. The presence of from 0.10 c.c. 1.22 S.G. sulphuric acid in the solution under estimation had no effect on the values obtained. It was possible, with a total volume of 25 c.c., to detect the point of disappearance of the blue colour to within 0.1 c.c. using titanous chloride as dilute as 1 c.c. = 0.00006 g. iron and, hence, to estimate as little iron as 0.006 mg. The volume of electrolyte used for titration varied from 1 c.c. to 10 c.c. according to the iron concentration in the electrolyte. A method for the micro-estimation of iron with titanous chloride has recently been described by Brukl,<sup>11</sup> who employs potassium thiocyanate as indicator. Solutions of this indicator were found to suffer serious deterioration with time and even fresh solutions were not entirely trustworthy, low titration values being obtained. A similar effect has been observed by other workers (Philip and Bramley<sup>12</sup>; Stokes and Cain<sup>13</sup>), but while this effect is negligible when using fresh solutions of the indicator and titrating iron solutions of more usual concentrations, it was sufficiently large, with the very dilute iron solutions dealt with here, to render the use of this indicator unreliable.

### Relations between Iron Concentration, Temperature and Rate of Self-Discharge.

*Positive Plates.*—The rate of self-discharge of groups of four cells (Type A) of varying electrolyte iron concentrations was measured at 0°, 23.9°, 32°, and 48.9° C., by the differences between the capacity obtained on discharge immediately following a charge, and that given on discharge after varying periods of standing at the given temperature. Cells were worked in water thermostats controlled to within 0.1°, but the actual cell temperatures on discharge rose about 1.0° above the thermostat temperature. The results are shown in Table I. The figures in brackets give, in each case, the difference in capacity between the cell concerned and the cell containing the lowest iron content when discharged after the same period of standing. The differences between the bracketed figures in any horizontal column, for

<sup>10</sup> "New Reduction Methods in Volumetric Analysis."

<sup>11</sup> *Microchemie*, 1, 54 (1923).

<sup>12</sup> *J. Chem. Soc.*, 103, 795 (1913).

<sup>13</sup> *J. Amer. Chem. Soc.*, 29, 409 (1907).

discharge after zero time of standing and for discharge after the indicated number of hours, give the self-discharge for that time at the given electrolyte iron concentration. As all these cells when containing pure electrolytes had equal capacities, the bracketed figures for zero time represent the permanent loss due to the indicated iron concentration. The figures for permanent loss are shown here for convenience, but their consideration is deferred to the second paper.

It must be noted that as these cells had about 70 per cent. excess negative plate capacity the results refer to the positive plate.

The data for  $0^\circ$  are not shown, as no self-discharge loss outside the limit of experimental error could be measured for cells containing up to 0.09 g. iron/100 c.c. and for periods of standing up to 14 days.

It is seen that, except at  $48.9^\circ$ , the iron concentration of the pure cell was sufficiently low to give no measurable self-discharge. During the 164-hour period of standing at  $48.9^\circ$ , the self-discharge loss of the pure cell was of the same order as the other cells, and no relation between iron content and self-discharge was observable. This was confirmed by subjecting another group of four cells to a period of standing of 7 days at  $48.9^\circ$ , with similar results. At this temperature the cells are subject to large capacity losses due to causes other than the presence of iron, and the self-discharge effect of this impurity is thereby masked. As

the cells do not appear to have been subject to so much abnormal loss during the 72-hour period of standing, an approximate figure for the rate of loss of capacity due to iron at this temperature may be obtained from the first two columns. The data contained in Table I are shown plotted in Figs. 1, 2, and 3. *It is seen that an approximately linear relation holds between iron content and self-discharge loss, but that the rate of loss tends to decrease with time.* In Fig. 4 the mean loss of capacity per day, as calculated from periods of standing up to 7 days, in a cell containing 0.08 g. iron/100 c.c. electrolyte, is shown as a function of temperature. This curve can only be regarded as a rough approximation, in view of the impossibility of measuring capacity losses accurately. The order of the loss has however been confirmed by a number of measurements.

*Self-Discharge at the Negative Plate.*—Cells of type A were employed with the two outside negative plates removed, thus leaving the cells with a

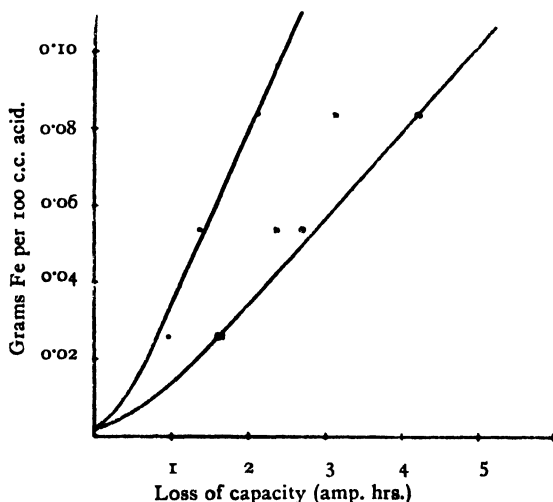


FIG. 1.—Temp.  $23.9^\circ$  C. Iron concentration/Loss of capacity.

• Immediate discharge.

× Values after 120 hours' standing.

[The lowest point (cell with 0.026 gm. Fe per 100 c.c.) is a very bad point, and consequently the curve for this time of standing has not been drawn.]

⊙ After 216 hours' standing

TABLE I.

Temp.	Discharge Rate.	Cell No.	Electrolyte Iron Conc. : g./100 c.c.	Capacity (in Amp. Hours) after Standing.		
				Immediate Discharge.	120 Hours.	220 Hours.
23°9'	3 amps.	1	0.084	19.9 (2.13)	18.77 (3.13)	17.55 (4.25)
		2	0.054	20.65 (1.38)	19.53 (2.37)	19.1 (2.70)
		3	0.026	21.08 (0.95)	20.27 (1.63)	20.2 (1.60)
		4	0.0018	22.03	21.90	21.8
32°	5 amps.				93 Hours.	168 Hours.
		1	0.081	17.2 (2.34)	15.4 (4.30)	14.67 (4.93)
		2	0.050	18.17 (1.37)	16.83 (2.87)	16.33 (3.27)
		3	0.024	18.83 (0.71)	18.40 (1.30)	17.67 (1.93)
48°9'	5 amps.	1	0.075	19.07 (2.72)	16.17 (3.91)	14.58 (2.59)
		2	0.042	20.08 (1.71)	17.34 (2.74)	15.25 (1.92)
		3	0.020	20.83 (0.96)	18.51 (1.57)	16.42 (0.75)
		4	0.0018	21.79	20.08	17.17

considerable excess positive capacity. The results of these measurements

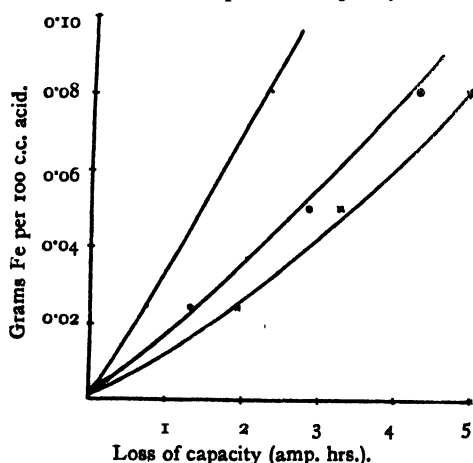


FIG. 2.—Temp. 32° C. Iron concentration/Loss of capacity.

- Immediate discharge.
- After 93 hours' standing.
- × After 168 hours' standing.

were only approximate owing to individual variations of cell-capacities, but the data obtained were sufficient to show that similar self-discharge losses occurred and that they were not widely different from those obtained with positive plates. These self-discharge losses should, according to the Dolezalek theory, be equal. In any case measurement of self-discharge losses in the negative plates is difficult, owing to the gradual loss of capacity of the negative plates in pure acid used as a standard. In the next section evidence is given showing that no abnormal re-action of the type postulated by Vinal and Altrup<sup>6</sup> takes place at the negative plate.

### The Effect of Iron on the Attack of the Negative Plate by the Acid.

The results of Vinal and Altrup with regard to the negative plate action have already been discussed. These workers suggested that the presence of iron catalyses the reaction given by equation (2b). The ultimate disappearance of this increased velocity might be explained by assuming that

the reaction was catalysed by *ferric* and not by *ferrous* iron, since in Vinal and Altrup's experiments the iron was being reduced to the ferrous condi-

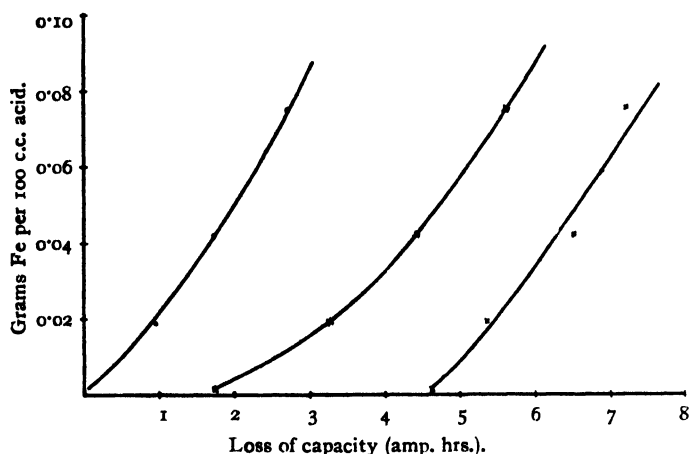


FIG. 3.—Temp. 48.9° C. Iron concentration/Loss of capacity.

• Immediate discharge.  
 × After 72 hours' standing.  
 + After 168 hours' standing.

tion. This reaction (2b) may be followed by measuring the rate of gas evolution.

Three segments of equal size and containing in each case 6.5 g. of paste were cut from a freshly charged negative plate, washed and soaked

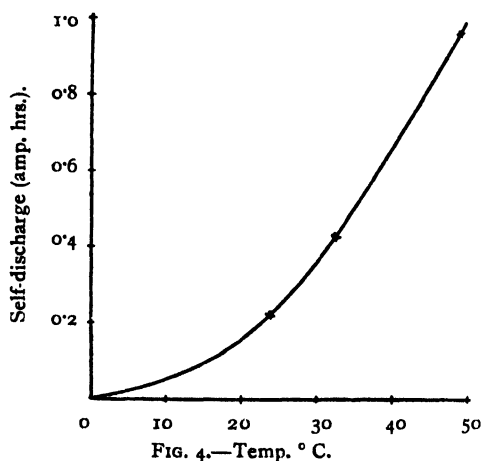


FIG. 4.—Temp. °C.

for a short time in distilled water, and one section immersed in each of the following solutions:—

- (1) Pure sulphuric acid 1.250 S.G.
- (2) Sulphuric acid 1.250 S.G. containing 0.08 per cent. iron as *ferric* sulphate.
- (3) Sulphuric acid 1.250 S.G. containing 0.08 per cent. iron as *ferrous* sulphate.

## 276 ACTION OF IRON AS IMPURITY IN LEAD ACCUMULATOR

The experiment was carried out in a thermostat at  $25^{\circ}$  and the gas evolved was collected in gas burettes, its volume being read at intervals. The results are shown in Table II, all gas volumes being reduced to *N.T.P.*

TABLE II.

C.C. HYDROGEN GAS EVOLVED AT *N.T.P.*

In—	0	20	65'25	96'5	137	161	188 hours.
Solution 1.	—	5'60	16'20	22'90	31'6	36'6	41'95
Solution 2.	—	5'61	16'12	22'90	31'4	36'0	40'9
Solution 3.	—	5'24	15'80	22'60	31'3	36'35	41'8

These results have been confirmed by a further similar experiment. It is seen that within the limit of experimental error the rates of gas evolution are the same in each case, except towards the end of the run, when slight irregularities occurred. In addition the data fall on a smooth curve, the rates of gas evolution slowly decreasing with time owing to a gradual reduction in the surface area of the unattacked lead. These results are in complete disagreement with the theory suggested by Vinal and Altrup. *It may be concluded that the normal action of iron on a negative plate is only that given by equation (2a).*

### Rate of Decrease of Self-Discharge with Time.

The electrolyte iron concentration of a cell of type B was made up to 0.91 g./100 c.c. in order to magnify the self-discharge losses. The cell was then allowed to stand for varying periods at laboratory temperatures (about  $18^{\circ}$ ) and the capacity on discharge was measured.

TABLE III.

Time of Standing in hours.	0	16'5	17	65	67'5	112'5	264	336	0
Capacity in Amp.-Hours.	13'1	10'2	10'6	7'6	7'95	6'43	2'0	1'55	12'55

The rate of loss of capacity is greatest initially and decreases with time, as is to be expected, since the self-discharge first takes place in the surface layers of the plates, but the point of action must gradually move further into the plates, increasing the distance through which the iron must migrate from one plate to another. In addition, the external lead sulphate coating hinders the penetration of the plate.

*Effect of Acid Renewal.*—The renewal of the acid in a cell has been found to decrease both the permanent loss and the rate of self-discharge in proportion to the percentage of contained iron thereby removed from the cell. As regards the self-discharge loss this result would naturally follow from the Dolezalek theory, but it is of interest to note that the permanent loss is also recovered.

### The Distribution of Iron in the Electrolyte.

Reference has already been made to the uneven distribution of the iron throughout the electrolyte of a cell. This distribution is largely dependent

on the history of the cell in the period immediately preceding the time at which measurements are made. In general a definite tendency exists for the accumulation of the iron at the bottom of the cell, this being the greater, within limits, the longer a cell stands without working. Discharge has but little effect on this distribution, but on charge there is a marked tendency for the iron concentrations over a cell to be equalised by the disturbance produced by gassing, although complete equalisation was not normally attained. In some cases a definite steady increase in iron concentration from the top of the cell downwards was observable, while in others the concentration was moderately uniform above the bottom of the plates, but below this level, in the dead space at the bottom of a cell, a considerably higher iron concentration existed. A few examples of the data obtained are given, concentrations being expressed as g. of iron per 100 c.c. electrolyte.

(1) Immediately after charge—Top of cell—0.0902.

7 days later. Cell standing in interval—

Top of cell . . . . . 0.0791

Bottom of cell . . . . . 0.0937

(2) A cell in regular daily working for a long period—

Top of cell . . . . . 0.0855

Bottom of cell . . . . . 0.094

(3) A cell after 12 days' standing discharged—

Top of cell . . . . . 0.087

Bottom of cell . . . . . 0.101

(4) Cell containing a mean electrolyte iron concentration of 0.91 g./100 c.c. after a period of working—

Top of cell . . . . . 0.880

Half-way down cell . . . . . 0.908

Bottom of cell . . . . . 0.961

The expression "Top of Cell" indicates that the sample was removed from within one or two cm. of the electrolyte surface; "Bottom of Cell" that the sample came from below the plates.

It must be pointed out that the variation obtained on any given operation was dependent on uncontrollable factors, but the data give an indication of the maximum differences found. In working cells a considerable difference in acid density exists between the top and the bottom of a cell, though again the magnitude of this difference is dependent on the previous history of the cell. Some typical figures for cells which had been standing charged about ten days are given.

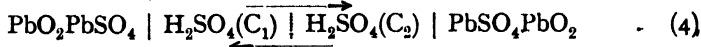
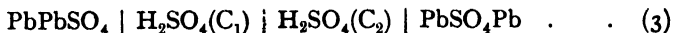
TABLE IV.  
ACID DENSITY.

Cell Number.	I.	II.	III.
Top of Cell . . . . .	1.205	1.215	1.192
Bottom of Cell . . . . .	1.210	1.232	1.220

This higher concentration of acid at the bottom of a cell is due to the action of charge, during which the concentrated acid produced in the pores of the plates falls down the plates towards the bottom of the cell, owing to its high specific gravity and the insufficient rapidity of mixing with the main bulk of the electrolyte. This action will be particularly marked at high

charging rates. When gassing commences, this action will cease, and the gas evolution will tend to equalise the acid concentrations throughout the cell, but will have little effect on the acid in the dead space below the plates.

The distribution of the iron in a cell may be explained as follows: The higher acid concentration existing at the bottom of a cell sets up the following concentration cells between the upper and the lower parts of the plates.



Assume  $C_1 > C_2$ . The arrows indicate the direction in which positive ions move under the influence of the concentration cell *E.M.F.* Taking the dissociation of sulphuric acid as  $\text{H}_2\text{SO}_4 = 2\text{H}^+ + \text{SO}_4^{2-}$ , the net transfer, if 2 faradays pass from left to right in (3), is  $n_e$  mols.  $\text{H}_2\text{SO}_4$  from  $C_1$  to  $C_2$ , while a similar current passing from right to left in (4) involves the transfer of  $(2 - n_e)$  mols.  $\text{H}_2\text{SO}_4$  from  $C_1$  to  $C_2$  and two mols. of water in the opposite direction.  $n_e$  represents the transport number of the cation. If the *E.M.F.* of these cells be represented by  $E_1$  and  $E_2$ , then neglecting the water transport in (4),

$$E_1 = 3/2 n_e \frac{RT}{F} \log \frac{C_1}{C_2}$$

$$E_2 = 3/2 (2 - n_e) \frac{RT}{F} \log \frac{C_1}{C_2}$$

For 7.6 *N* sulphuric acid (1.224 S.G. at 18°)  $n_e = 0.785^{14}$  at 19°, so that,

$$E_1 = 1.177 \frac{RT}{F} \log \frac{C_1}{C_2}$$

$$E_2 = 1.822 \frac{RT}{F} \log \frac{C_1}{C_2}$$

Now in (3) the positive ions move from the stronger to the more dilute acid, and the reverse holds in (4). Since  $E_2 > E_1$  the equalisation of acid concentration would, if these concentration cells were isolated, occur more rapidly in (4) than in (3), but actually the horizontal distance between plates is small compared with their depth, and ordinary diffusion processes will ensure that  $C_1$  has always approximately the same value at any one horizontal plane, and similarly  $C_2$ . The net downward *E.M.F.*, this being assumed to

act on all the ions between the two plates, is  $E_2 - E_1 = 0.645 \frac{RT}{F} \log \frac{C_1}{C_2}$

and this leads to a net transfer of ferrous and ferric ions in this direction. An accumulation of iron at the bottom of the cell will therefore occur. The acid concentration at the bottom of a cell will be renewed to a higher value by the action of every charge (unless prolonged gassing occurs), and hence in a working cell the presence of a higher concentration of iron at the bottom than the top is to be expected. This theory is sufficient to account quantitatively for the order of the differences obtained.

The distribution of the iron between the ferrous and ferric states has also been studied and the result shows, as is to be expected, that the iron in immediate contact with the positive plate is in the ferric state while that in

<sup>14</sup> Landolt Börnstein, *Phys. Chemische Tabellen* (1923), 1104.

contact with the negative plate is in the ferrous state. The main bulk of the solution outside the plates always showed a considerable excess of ferrous iron over ferric iron, but this appears to be due to the outside plates being negatives, as with cells in which the outside plates were positives the reverse was found.

### Internal Resistance of the Cell and Plate Potentials.

The internal resistance of cells with varying iron contents has been measured by the method due to Carhart,<sup>15</sup> but no consistent differences have been obtained. The internal resistance of cells of type A varied between 0.033 and 0.05 ohms, but were in no way related to the cell iron contents. Plate potentials have also been measured against mercurous sulphate electrodes ( $7.6 \text{ NH}_4\text{SO}_4$ ) for various electrolyte iron contents, but again no consistent differences due to this impurity have been observed.

### Calculation of Self-Discharge.

The reactions at the positive and negative plates are given by equations (1) and (2a) and at each plate a definite equilibrium will exist corresponding to the plate potential. For the *E.M.F.* of a ferrous-ferric electrode  $E = E_0 - \frac{RT}{F} \log \frac{(\text{Fe}^{II})}{(\text{Fe}^{III})}$ , where  $E_0$  is the normal potential, 0.713 volts.<sup>16</sup> The potentials of the positive and negative plates of a lead cell in 1.22 S.G. sulphuric acid are + 1.72 volts and - 0.34 volts approximately (all potentials are quoted on the hydrogen scale). Hence it may be calculated

$$\begin{aligned} \text{that at the positive plate } (\text{Fe}^{II})/(\text{Fe}^{III}) &= 10^{17.4}, \\ \text{and at the negative plate } (\text{Fe}^{II})/(\text{Fe}^{III}) &= 10^{18.2}. \end{aligned}$$

Concentration gradients of  $(\text{Fe}^{II})$  and  $(\text{Fe}^{III})$  will then exist between the plates in opposite directions.<sup>17</sup>  $\text{Fe}^{II}$  will diffuse from negative to positive plate where it is oxidised to  $\text{Fe}^{III}$  and will then diffuse back to the negative plate, be reduced to  $\text{Fe}^{II}$ , and commence the cycle again. Assuming this cycle, as required by the Dolezalek theory, it is possible to calculate the rate of self-discharge under given conditions.

Consider  $\text{Fe}^{II}$  and  $\text{Fe}^{III}$  diffusing independently under the influence of their own concentration gradients and as (a) all undissociated or (b) as completely dissociated but each ion carrying equivalent amounts of  $(\text{SO}_4^{II})$  ions along with it. For the purpose of calculating the concentration gradients the concentrations of  $(\text{Fe}^{II})$  and  $(\text{Fe}^{III})$  will be taken as zero at the plates towards which they are diffusing. Concentrations are expressed as gram atoms/c.c. Let the cross sectional area be  $A \text{ cm}^2$  and the distance between the plates  $a \text{ cms}$ . Let  $c_0^{II}$  and  $c_0^{III}$  represent the concentrations of  $\text{Fe}^{II}$  and  $\text{Fe}^{III}$  at the plates at which they are produced,  $k$  and  $(1 - k)$  the fraction of total iron in the ferrous and ferric states respectively, and  $C$  the total iron concentration. It is assumed that an ion reacts immediately it reaches a plate.

The quantity of a solute crossing any plane in a given time is, from Fick's law, proportional to the concentration gradient. Now in equilibrium the same number of  $\text{Fe}^{II}$  (or  $\text{Fe}^{III}$ ) ions must cross any plane parallel to the plates in a given time. Similarly the number of ions arriving at either

<sup>15</sup> *Physical Rev.*, **2**, 392 (1894-95).

<sup>16</sup> Peters, *Z. physik. Chem.*, **26**, 193 (1898).

<sup>17</sup>  $(\text{Fe}^{II})$  and  $(\text{Fe}^{III})$  refer to total salt concentrations and  $(\text{Fe}^{II})$  and  $(\text{Fe}^{III})$  to ionic concentrations.

electrode in a given time must be equal to the number departing (in of course a different valency state). Hence both the  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  concentration gradients must be linear and the concentration of  $\text{Fe}^{\text{II}}$  at the negative plate will be twice its mean concentration, *i.e.*

$$c_0^{\text{II}} = 2kC \text{ and similarly } c_0^{\text{III}} = 2(1 - k)C.$$

Applying Fick's law to either species,

$$dS_{\text{II}} = -D_{\text{II}}A\left(-\frac{2kC}{a}\right)dt$$

$$dS_{\text{III}} = -D_{\text{III}}A\left(-\frac{2(1 - k)C}{a}\right)dt$$

where  $S_{\text{II}}$  and  $S_{\text{III}}$  represent the amount of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  respectively, crossing any plane in time  $t$ , and  $D_{\text{II}}$  and  $D_{\text{III}}$  are the diffusion constants for  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  respectively. Now in equilibrium  $dS_{\text{II}} = dS_{\text{III}}$

therefore

$$k = \frac{D_{\text{III}}}{D_{\text{II}} + D_{\text{III}}}$$

$$dS_{\text{II}} = dS_{\text{III}} = -D_{\text{II}}A\frac{(-2D_{\text{III}}C)}{a(D_{\text{II}} + D_{\text{III}})}dt,$$

or

$$S_{\text{II}} = S_{\text{III}} = \frac{2AC}{a} \frac{D_{\text{II}}D_{\text{III}}}{D_{\text{II}} + D_{\text{III}}} \quad (5)$$

The assumption that the ferrous and ferric ions diffuse independently of one another, each carrying equivalent amounts of  $(\text{SO}_4^{--})$  with it, was necessarily made for simplicity but an alternative interdependent diffusion is more probable, the transfer consisting of  $2 \text{Fe}^{++}$  in one direction across any plane and  $2 \text{Fe}^{+++}$  ions in the opposite direction, together with the appropriate number of hydrogen or sulphate ions in the direction required to maintain electrical equilibrium. The treatment of this case, however, leads to no solution as four variables  $c^{\text{II}}$ ,  $c^{\text{III}}$ ,  $\frac{dc^{\text{II}}}{dx}$ , and  $\frac{dc^{\text{III}}}{dx}$  are involved and only two connecting equations can be obtained on theoretical grounds. The only method of solution in this case would seem to be the experimental measurement of  $c^{\text{II}}$  and  $c^{\text{III}}$  at various points between widely spaced electrodes, and the formulation of empirical equations connecting these results with  $\frac{dc^{\text{II}}}{dx}$  and  $\frac{dc^{\text{III}}}{dx}$ . The case when the ferrous and ferric sulphates are considered as only partially dissociated is more complex and leads to no solution. On the basis of the electrode reactions previously stated the self-discharge by iron leads to acid dilution at the electrodes and hence, whatever mechanism of the diffusion process be considered, an acid concentration gradient will be set up. This gradient may act either from negative to positive plate or from midway between the plates to the plates, according to the mechanism of the diffusion process assumed.

In the case of a completely ionised solute the diffusion constant may be calculated from the expression,

$$D = RT \frac{U_a U_c}{U_a + U_c} \left( \frac{1}{v_c} + \frac{1}{v_a} \right) \quad (6)$$

where  $v_a$  and  $v_c$  represent the valencies of anion and cation respectively, and  $U_a$  and  $U_c$  the corresponding mobilities when unit force acts on one equivalent weight of ions. This expression however only holds for the

normal case when anion and cation are under the same concentration gradient.

In the case under consideration the anion gradient will either oppose diffusion of anions from positive to negative plate and assist in the reverse direction, or, as is more probable, will oppose the motion from the plate to midway between the plates for ions travelling in either direction and assist the motion for the remaining half of the path. The net effect of the acid gradients is therefore small compared with that of the ferrous and ferric iron gradients, and the whole may be considered as a case of diffusion due to a concentration gradient acting on the cations only.

The following modified expression may be deduced for the case where the cation is under a concentration gradient, but no such gradient acts on the anion.

$$D = RT \frac{U_a U_c}{U_a + U_c} \cdot \frac{1}{v_c} \quad (7)$$

Taking the day as unit of time  $D$  may be calculated after conversion of all terms into the same system of units. At  $18^\circ$  for ferrous sulphate<sup>14</sup>  $U_a = 68$ ,  $U_c = 45$ , and for ferric sulphate  $U_a = 68$ ,  $U_c = 61$ .

Hence  $D_{II} = 0.303$  and  $D_{III} = 0.240$  (neglecting the viscosity correction). For the case when the salts are completely undissociated  $D = \mu RT$  where  $\mu$  is the velocity when unit force acts on 1 gram molecule. This expression cannot be evaluated since  $\mu$  is unknown. Haskell<sup>18</sup> found for the case of two salts investigated that

$$D_{\text{undissociated}} = \frac{1}{2} D_{\text{dissociated}} \text{ approximately.}$$

Calculating  $D_{\text{dissociated}}$  from equation (6) the values 0.607 and 0.60 are obtained for ferrous and ferric sulphates respectively and, hence, the corresponding undissociated salt values would be 0.303 and 0.30. The values of the diffusion constants for the ions and the undissociated salts are not widely different and for the calculation of self-discharge the former have been used.

The transfer of one gram atom of iron to each plate results in a discharge of one faraday or 26.8 amp. hours and thus from equation (5)

$$\text{Self-discharge} = \frac{2AC}{a} t \frac{D_{II}}{D_{II} + D_{III}} \frac{D_{III}}{D_{II} + D_{III}} 26.8 \quad (8)$$

For cells of type "A" the plate area is  $9.75 \times 10.2 \text{ cm.}^2$  and  $a = 0.5 \text{ cm.}$  and, since these are five plate cells, there are four such diffusion areas. A correction may also be applied for the marginal effects on the basis of some results for marginal conductivities given by Ahmed.<sup>19</sup> The marginal spaces were, at sides of plates 0.35 cm., at top of plates 0.5 cm., and below plates 1.5 cm. The increase of conducting area and hence of diffusion area due to these margins is small, being about 8 per cent. approximately. The total diffusion area is therefore  $4 \times 9.75 \times 10.2 \times 1.08 \text{ cm.}^2$ , and the self-discharge per day at  $18^\circ$  from (8) = 6170 C. For the case of an iron concentration of 0.08 g./100 c.c.,  $C = 1.4 \times 10^{-5}$ , so that the self-discharge per day at  $18^\circ = 0.086$  amp. hours. The experimental value, as obtained from Fig. (4), is 0.12. The order of agreement is as good as can be expected in view of the non-rigorous treatment necessarily adopted.

<sup>18</sup> *Physical Rev.*, **27**, 145 (1908).

<sup>19</sup> *J. Inst. Elec. Eng.*, **62**, 301 (1924).

### Summary.

1. The presence of iron as an impurity in the lead accumulator has been found to cause a self-discharge of both positive and negative plates to the same extent, and also to produce an additional permanent loss in capacity at the positive plate. No other effect on the life or performance of cells has been found.
2. The rates of self-discharge of cells have been measured for various temperatures and electrolyte iron concentrations, and the results have been shown to be in general agreement with the Dolezalek theory of the self-discharge. The rate of self-discharge is proportional to the electrolyte iron concentration and increases with temperature.
3. The titanous chloride method for determination of iron has been adapted to the estimation of small traces of iron in sulphuric acid solution.
4. A variation of iron concentration in different parts of the electrolyte has been observed. This has been connected with the existence of acid concentration cells between different parts of the plates.
5. The reaction of iron at the negative plate has been studied. The results of Vinal and Altrup are not wholly confirmed.

## PART II. PERMANENT CAPACITY LOSS. ADSORPTION AND DESORPTION OF THE IRON BY THE POSITIVE PLATE.

Evidence has been presented in the previous paper that the presence of iron in a lead cell leads to a permanent loss in capacity, (that is, the capacity of the cell when discharged immediately after charging is lowered), and also that the iron is adsorbed by the positive paste. In the present paper the nature of, and relation between, these effects is described.

### Permanent Capacity Loss.

The permanent loss occurring in a cell containing iron has been found to be dependent on the iron content of the cell, the temperature and the rate at which the cell is discharged. The relations between permanent loss and electrolyte iron concentration at 23.9°, 32°, and 48.9° C. are given by the curves for zero time of standing in Figs. 1, 2 and 3 of Part I. The time of discharge, for the pure cell in each case, was 7.30, 3.92, and 4.36 hours respectively for the 23.9°, 32°, and 48.9° curves. These curves show that an approximately linear relation holds between the electrolyte iron concentration and the permanent loss, except possibly at low iron concentrations ( $< 0.02$  g./100 c.c.). Further measurements of permanent loss have been carried out by determining the capacities of cells, when containing pure electrolyte, at various temperatures and discharge rates and then redetermining these values after the addition of given amounts of iron to the electrolyte. The electrolyte iron concentrations given are the values obtained after the equilibrium between the positive paste and electrolyte had been established. In the following Table the permanent losses are quoted as percentages of the cell capacity at the rate concerned when containing pure electrolyte. The cells employed for these measurements were of type A (see Part I.). Numbers 2, 6, 13 and 14 are interpolated and extrapolated values taken from Figs. 1, 2, and 3 of Part I. It is seen that the permanent loss decreases as the discharge rate increases for a given temperature and iron

TABLE I.

Number.	Temperature °C.	Discharge Rate, Amps.	Time of Discharge, Hours.	Electrolyte Iron Conc.: g./100 c.c.	Permanent Loss Per Cent.
1	0	3	4.63	0.149	5.75
2	23.9	3	7.34	0.052	6.8
3	23.9	3	6.30	0.052	5.3
4	23.9	4	5.14	0.052	5.0
5	23.9	5	3.01	0.052	4.0
6	23.9	3	7.34	0.110	12.2
7	23.9	3	6.34	0.109	10.75
8	23.9	5	2.97	0.109	6.7
9	23.9	8	1.72	0.109	5.4
10	32	3	7.10	0.110	11.5
11	32	5	3.44	0.110	9.9
12	32	8	2.01	0.110	8.7
13	32	5	3.91	0.110	14.3
14	48.9	5	4.36	0.110	17

concentration. The 23.9° data fall on a smooth curve but those at 32° are more irregular, in particular No. 13 seems high while No. 10 is low. In Fig. (1) the permanent loss at the 4.5 hour rate of discharge is shown plotted against temperature for an electrolyte iron concentration of 0.11 g./100 c.c. The value at 0° (No. 1, Table I.) has been corrected to an iron concentration of 0.11 g./100 c.c., assuming the linear relation between electrolyte iron concentration and permanent loss. Two further approximate values (not plotted) of 7.1 per cent. at 18° and 7.8 per cent. at 17°, which were obtained

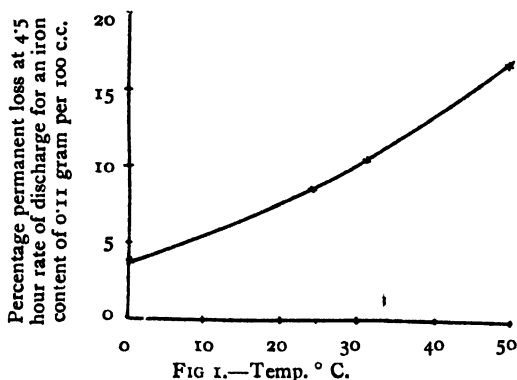


FIG 1.—Temp. °C.

from other data, are in good agreement with this curve. Cells of type B containing Semi-Plante positive plates, appear to show somewhat larger permanent losses than those obtained with pasted plates, but no accurate measurements on such plates have been made. The linear relation between electrolyte iron concentration and permanent loss breaks down when very high iron concentrations are reached. A cell containing 0.91 g. Fe/100 c.c. showed a permanent loss of about 33 per cent. at 18° when discharged at the six hour rate, while the linear relation required a loss of about 70 per cent. under those conditions.

### The Iron Adsorption at the Positive Plate.

The changes occurring in the total iron content of the electrolyte of a cell containing iron are masked to a large extent by the uneven distribution of the iron between different parts of the electrolyte, unless this be mixed before withdrawing samples for analysis. All electrolyte iron concentrations given in this paper are mean values thus obtained. It has been found

## 284 ACTION OF IRON AS IMPURITY IN LEAD ACCUMULATOR

that the iron in the electrolyte is adsorbed at the positive plate and that an equilibrium, dependent on the temperature and the acid concentration, is established between electrolyte and positive paste iron concentrations.

The progressive drop which occurs in the mean iron concentration of a cell, from the time of addition of the iron, may be illustrated by the following data (at 18°):—

TABLE II.

Time after addition of iron (days)	1	9	54	125
Electrolyte Iron Conc: g./100 c.c.	0.0342	0.0317	0.0302	0.0307

The last two values are in agreement within the limit of experimental error and show that an equilibrium is reached. This conclusion has been confirmed by many other similar results.

The influence of temperature on this equilibrium is shown for some cells of type A. The initial iron concentrations are only approximate, as the exact electrolyte volume of any particular cell was unknown.

TABLE III.

Cell Number.	1	2	3
Initial iron concentration of electrolyte g./100 c.c.	0.033	0.062	0.1
Equilibrium iron concentration of electrolyte at 18° g./100 c.c.	0.028	—	0.087
Equilibrium iron concentration of electrolyte at 48.9° g./100 c.c.	0.0195	0.040	0.070

The final equilibrium values at 48.9° were confirmed by further experiments on other cells of the same type made up to similar initial iron concentrations, and good agreement was found. In order to identify the solid phase which was taking part in this equilibrium a cell which had attained equilibrium at 48.9° was analysed throughout, *i.e.* positive and negative paste, separators and electrolyte. The pastes were analysed after being soaked in distilled water for two hours, dried and weighed. In all cases the amount of iron found in the wash waters was small and only of the order which might be attributed to the electrolyte in the section before washing, the approximate volume of this being known. The values found were:—

Negative paste, 0.0044 per cent. of iron. Weight of negative paste in cell, 350 g. Total iron in negative paste = 0.015 g. Positive paste, 0.041 per cent. of iron. Weight of positive paste in cell 300 g. Total iron in positive paste = 0.123 g. Wood Separators: The analysis was carried out on a wet weighed sample. The iron content was approximately equal to that of the acid volume held by the section, and hence the iron content of the separator is negligible. Electrolyte, 0.0195 g. iron/100 c.c. Volume of electrolyte, 750 c.c. Total iron in electrolyte = 0.146 g. Total iron found in cell = 0.284 g. This cell initially contained 0.085 g. and had 0.196 g. of iron added to it. Total iron in cell = 0.281 g. The agreement is satisfactory. This cell had an initial electrolyte iron concentration of 0.033 g./100 c.c., and the above result shows that the decrease in this value is accounted for by the increased iron content of the positive paste. In the following Table the results of a series of analyses of electrolytes and positive pastes of cells which had attained equilibrium at the temperature given are shown.

TABLE IV.

Type Cell.	Temperature, °C.	Electrolyte Iron Conc.: g./100 c.c.	Positive Paste Iron Conc.: Per Cent.
B	18	0.00051	0.0041
A	18	0.005	0.012
B	18	0.029	0.026
B	18	0.0535	0.0406
B	18	0.092	0.0645
A	48.9	0.0018	0.0161
A	48.9	0.0195	0.041
A	48.9	0.0403	0.056
A	48.9	0.0698	0.073

The values of electrolyte iron concentration are plotted against positive paste iron concentration in Fig. (2) and the logarithms of these values in Fig. (3). The latter fall on a straight line at 48.9° and, approximately so, at 18°, indicating that the adsorption over the range measured follows the

usual relation  $C_{\text{solid}} = a C_{\text{electrolyte}}^{\frac{1}{n}}$ .

It may be noted that except for low iron concentrations a roughly linear relation holds for the former curves. The shift of the equilibrium with temperature change is also shown by the curves. It appears doubtful, however, whether the spacing of the curves is an accurate measure of the change in the equilibrium with temperature. Analyses of pastes from the interior of plates of type B showed a lower iron concentration than that obtained for the surface paste. These plates were of the semi-Plante type, and the interior paste probably never reached its true equilibrium owing to the lack of porosity. All analysis given in the above table for type B cells were, however, carried out on the exterior paste which may be expected to be in true equilibrium. The values for type A cells are mean values for the whole paste and if, even at 48.9°, complete equilibrium throughout the paste is not reached the results will be low. Hence the spacing of the curves may be slightly too small owing to the 48.9° values being lower than the true equilibrium values.

In order to elucidate the influence of the electrical working and, also, of acid density, a series of experiments on the adsorption of iron by lead peroxide from sulphuric acid solutions of ferric sulphate was carried out. The lead peroxide was taken from a freshly charged positive plate (iron content 0.006 per cent.) which was washed in successive changes of distilled water until almost acid free, and dried in air at laboratory temperature. The paste was then removed and ground up and its free acid content estimated. Weighed samples of this lead peroxide were introduced into small flasks together with 25 c.c. of a sulphuric acid-ferric sulphate solution, and these were maintained in a thermostat at 25° until equilibrium was reached, the flask being shaken periodically. In the following Table are

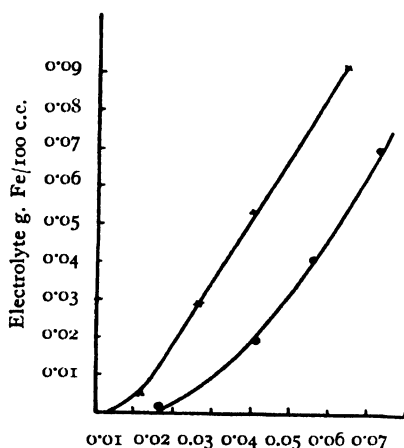


FIG. 2.—Positive paste % Fe.

x Isotherm at 18° C.

o Isotherm at 48.9° C.

shown the initial and final iron concentrations of the solution, the acid concentration (after correction for the free acid introduced by the lead-peroxide—this being 0.0039 g. sulphuric acid per g. lead-peroxide—but not for any acid produced by hydrolysis of the ferric sulphate\*) and other necessary data.

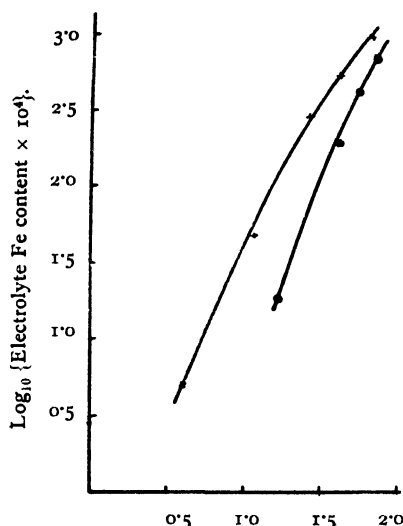


FIG 3.— $\text{Log}_{10}$  {Positive paste Fe content  $\times 10^3$ }.

$\times$  Isotherm at  $18^\circ \text{C}$ .

$\odot$  Isotherm at  $48.9^\circ \text{C}$ .

The great influence of acid concentration on the adsorption is clearly shown. It must also be noted that the adsorption is much less than occurs in the working cell at similar acid concentrations, this probably being due to the treatment accorded to the lead-peroxide before its use in the above experiments.

It is also shown by other data that the adsorptive power of lead peroxide decreases with age.

The influence of charge and discharge on the iron equilibrium in a cell and the changes taking place on raising the temperature have also been followed by the variations in the electrolyte mean iron concentration. Table VI. shows the influence of charge and discharge on cells

which had reached equilibrium, *i.e.* when further complete cycles of charge and discharge did not further alter the iron concentration for any one state

TABLE V.

No.	Grams Lead Peroxide.	Acid Conc. of Solution <i>N</i> .	Initial Solution Iron Conc.: g./100 c.c.	Final Solution Iron Conc.: g./100 c.c.	Drop in Solution Iron Conc. g./100 c.c.
1	5	0.0160	0.0875	0.0557	0.0318
2	5	0.0415	0.0875	0.0610	0.0265
3	5	0.1207	0.0875	0.0670	0.0205
4	5	0.488	0.0875	0.0752	0.0123
5	5	0.488	0.0875	0.0772	0.0103
6	5	1.65	0.0875	0.0828	0.0047
7	5	1.65	0.0875	0.0818	0.0057
8	5	3.32	0.0875	0.0842	0.0033
9	5	3.32	0.0875	0.0835	0.0040
10	5	6.78	0.0875	0.0854	0.0021
11	5	6.78	0.0889	0.0875	0.0014
12	1	0.0032	0.0875	0.0790	0.0085
13	1	0.0287	0.0875	0.0809	0.0066
14	1	0.1079	0.0875	0.0838	0.0037

of charge. The cells were of type A and the temperature  $18^\circ$ . The time at which analyses were made is shown in the Remarks Column.

Two complete cycles of charge and discharge are shown in the Table and it is seen that the solution iron concentration exhibits complete cycles.

\* Complete hydrolysis of a ferric sulphate solution of 0.0875 g. iron/100 c.c. would produce an 0.047 *N* acid solution.

TABLE VI.

Operation No.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Remarks.	1 Hour after Completion of Charge.	3 Days after (1).	2 Hours after Discharge.	3 Days after (3).	1 Hour after Charge.	8 Days after (5).	23 Days after (5).	4 Days after Discharge.	2 Hours after Charge.
Iron con- Cell No. 1	0.1134	0.1106	0.1098	0.1080	0.1142	0.1106	0.1109	0.1074	0.1135
centration of Electro- " 2	0.0601	0.0584	0.0574	0.0571	0.0600	0.0578	0.0580	0.0558	0.0596
lyte (g./100 c.c.) " 3	0.0919	0.0909	0.0880	0.0867	0.0931	0.0899	0.0890	0.0861	0.0926

These variations are not attributable to the volume change of the electrolyte on discharge. For cells of this type the electrolyte volume decreases about 1.5 per cent. on discharge and increases by a similar amount on charge. This would produce fluctuations in the opposite direction to those observed and therefore the actual effect of charge and discharge, apart from the volume change, is to produce changes in the iron concentration of the solution which are 1.5 per cent. greater than those given by the tabulated data.

The further adsorption which occurs to a new equilibrium state on raising the temperature to 32° was followed on the above cells, (2) being raised to 32° immediately after charging, (1) 6 days after charge and (3) immediately after discharge (and seven days after the preceding charge). Cell (2) dropped almost to its new equilibrium value within three days after increasing the temperature to 32° and without further electrical working. Cell (1) dropped to 0.111 during the six days standing at 18°, and within three days after raising to 32° reached 0.107, but no further drop occurred on standing five more days. Discharge had little effect, but on subsequent charge this cell dropped to 0.104 and, after one more complete cycle, reached its final equilibrium value 0.103. These results show the effect of age on the adsorptive power of the lead-peroxide, that which is not newly formed being incapable of adsorption to its correct value, and equilibrium being only reached by reforming the lead-peroxide after a complete cycle. Cell (3) dropped on standing at 32° to its normal 18° discharge value (0.087), but after subsequent charge it reached its final equilibrium value 0.083, thus confirming that freshly formed lead-peroxide is necessary for complete adsorption to occur. No variations in the electrolyte iron concentration were observable at this temperature (32°) outside the limit of experimental error. On lowering the temperature to 18° again the cyclic changes in electrolyte iron concentration recommended as before, after desorption to the equilibrium state had occurred.

### Desorption of Iron from the Positive Plate.

Desorption experiments have been carried out by changing the electrolyte of a cell and refilling with pure acid at constant temperature and, also, by lowering the temperature at which a cell was working.

(a) *Desorption Due to Drop in Temperature.*—A group of three cells which had attained equilibrium at 48.9° were fully charged at this temperature and then the temperature lowered to 18°. No appreciable desorption

## 288 ACTION OF IRON AS IMPURITY IN LEAD ACCUMULATOR

occurred on allowing the cells to stand four weeks without electrical working, as is shown by the following results.

TABLE VII.

Cell No. 1.	1.	2.	3.
Equilibrium iron concentration at 48°9' (g./100 c.c.)	0.0683	0.0391	0.0189
Iron concentration after 4 weeks at 18° (g./100 c.c.)	0.0685	0.0400	0.0193

A series of discharges and charges was then performed on these cells at 18°, the mean iron concentration of the electrolyte being estimated after each operation.

TABLE VIII.

Cell No. .	1.	2.	3.
Initial iron concentration (g./100 c.c.)	0.0685	0.0400	0.0193
Iron concentration after first discharge (g./100 c.c.)	0.0753	0.0452	0.0217
Iron concentration after first charge (g./100 c.c.)	0.0781	0.0476	0.0223
Iron concentration after second discharge (g./100 c.c.)	0.0805	0.0490	0.0238

Desorption was therefore produced only by the electrical working of the cells. This was confirmed by results obtained on two other cells which were lowered from 32° to 18°, no appreciable desorption taking place on standing, either with a cell which was freshly charged, or for one which was charged three days before the temperature was lowered. Experiments on two cells which were completely discharged and lowered from 32° to 18° showed that considerable desorption occurred on standing at 18°, the desorption process being finally completed by electrical working.

(b) *Desorption on Acid Change.*—The progress of the desorption was followed as before by estimations of the mean electrolyte iron concentration. Cells of type B were used. The complete history of the cells, following the acid change, until equilibrium was reached is shown in the following tables. The letters D or C in the remarks column indicate respectively that a cell was discharged or charged in this interval.

The acid held by the plates and separators in these cells was about 10 per cent. of the total electrolyte volume and hence, if no desorption occurred, the iron concentration would be reduced to about 10 per cent. of its previous value. Cell (1) showed a slow rise in electrolyte iron concentration for about four weeks after acid change and then did not rise further on standing. The time taken for this slow rise is too large to attribute it merely to a slow diffusion of the old acid from the plates and must be considered as a slow desorption. This process ultimately stopped and subsequent discharge gave a large rise in the iron concentration, which was further increased on subsequent electrical working until equilibrium was reached. The greater part of the adsorbed iron was therefore only desorbed by electrical working, and it is clear that the *iron adsorption is mainly irreversible*. The results from cells 2, 3 and 4 confirm this conclusion; e.g. when partial desorption by electrical working had occurred, the cells on standing rise to a steady value which, though not affected by further standing, is increased on subsequent working. It may also be noted that two cycles were sufficient to effect the greater part of the desorption, about 75

TABLE IX.—CELL NO. 1. ACID CHANGED WITH CELL IN CHARGED STATE.

Days after acid change	—	2	3	24	31	50	51	57	58 to 62	69	70 to 80	83	84 to 88	92	93 to 98	106
Remarks	Before acid change	No electrical working in this period														
Iron conc. of electrolyte (g./100 c.c.)	0.089	0.0095	0.0100	0.0111	0.0113	0.0113	—	0.0126	—	0.0137	—	0.0140	—	0.0144	—	0.0143

TABLE X.—CELL NO. 2. ACID CHANGED WITH CELL IN CHARGED STATE.

Days after acid change	—	2	2	2	3	3	3 to 4	4	6	24	50	105 to 110	112 to 117	121 to 128	123 to 128	131
Remarks	Before acid change	—	D.	—	C.	—	D.	—	C.	—	—	D.C. D.C. D.C.	D.C. D.C. D.C.	—	D.C. D.C. D.C.	—
Iron conc. of electrolyte (g./100 c.c.)	0.089	0.0082	—	0.0095	—	0.0111	—	0.0114	—	0.0133	0.0133	—	0.0145	—	0.0149	0.0148

TABLE XI.—CELLS NOS. 3 AND 4. ACID CHANGED WITH CELL IN DISCHARGED STATE.

Days after acid change	—	—	2	2	2	2	3	5	5 to 6	6	6 to 7	34	53	53 to 59	60 to 67	72 to 82	74 to 85
Remarks	—	Before acid change	—	—	C.	—	D.	—	C.	—	C. D. C.	—	—	D.C. D.C. D.C.	D.C. D.C. D.C.	—	—
Iron conc. of electrolyte (g./100 c.c.)	3	0.093	0.0096	—	0.0118	—	0.0131	—	0.0140	—	0.0148	0.0148	0.0158	—	—	0.0162	0.0161
	4	0.031	0.0032	—	0.0044	—	0.0048	—	0.0051	—	0.0055	0.0054	0.0054	—	—	0.0062	0.0062

per cent. at least of the adsorbed iron being thereby desorbed. This was further confirmed by analysis of the positive paste of a cell (5) after two cycles following acid change. The electrolyte iron concentration before acid change was 0.09 g. iron/100 c.c. and after two cycles following this change 0.0093 g. iron/100 c.c. The positive paste iron content then found was 0.0194 per cent. while its value before acid change was 0.064 per cent. (Fig. 2) and its equilibrium value for an electrolyte concentration of 0.0093 g./100 c.c. is 0.015 per cent. In two cycles this cell had desorbed to almost its new equilibrium condition.

Positive paste analyses were carried out on cells 1, 2, and 3 after equilibrium had been reached to determine if the same equilibrium was reached on desorption as on adsorption. In the following Table the experimental values are shown together with the value corresponding to the equilibrium electrolyte concentration as taken from Curve (2).

TABLE XII.

Cell No. .	1.	2.	3.
Positive paste iron concentration	Per Cent.	Per Cent.	Per Cent.
(a) Found . . . .	0.0182	0.016	0.022
(b) From Fig. (2) . .	0.019	0.0185	0.020

It may be concluded that the same equilibrium is reached in either direction, the small differences being due most probably to temperature fluctuations, as these cells 1, 2, and 3 were maintained at laboratory temperatures. The increase in the electrolyte iron concentration in these experiments is somewhat less than that calculated from the decrease in paste iron content, thus confirming the suggestion made earlier that the inner paste does not come into complete equilibrium in these semi-Plante type plates at 18°.

### Adsorption and Desorption Theory.

It has been shown by Carrara and Vespignani<sup>20</sup> that ferric sulphate is considerably hydrolysed in aqueous solution. At 25° and at a dilution of 1 g. mol./40 litres, hydrolysis to the extent of about 22 per cent. occurs and at lower concentrations the hydrolysis is still greater. The hydrolysis of ferric chloride has been more extensively studied,<sup>21</sup> and it is probable that the hydrolysed product exists as complex positively charged ions of a colloidal nature. The presence of a high concentration of sulphuric acid will drive back this hydrolysis, but a certain amount of the hydrolysed product will exist in equilibrium with the acid solution. The adsorption of iron, when manganese dioxide is precipitated by the addition of ammonium persulphate to an acid solution of manganous sulphate containing iron salts, has been studied by Geloso<sup>22</sup> who found that the iron is mostly adsorbed as the hydroxide and also that there is a parallelism between the increase of hydrolysis of ferric sulphate on dilution and the adsorption results. The adsorption was also found to decrease as the acid concentration was increased, this variation following an exponential rather than a linear function. The results obtained in the present investigation show that with increasing

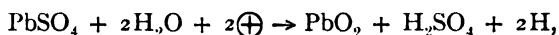
<sup>20</sup> *Gazetta*, 30, ii, 50 (1900).

<sup>21</sup> Goodwin, *Z. physikal. Chem.*, 1896, 21, 1; Malfitano and Michel, *Compt. Rend.*, 1907, 145, 185, 1275; Quartaroli, *Gazetta*, 45, i, 139 (1915). The authors desire to express their thanks to the Director of Scientific Research, Admiralty, for directing their attention to the above papers with the suggestion that it was the hydrolysed product which was adsorbed.

<sup>22</sup> *Compt. Rend.*, 1922, 174, 1629.

acid concentration the adsorption rapidly diminishes, and the curve obtained by plotting these results is very similar to that obtained by Geloso. It may therefore be concluded that it is the hydrolysed ferric iron existing as a complex ion which is adsorbed. The rapid increase in the hydrolysis of the ferric salt with temperature<sup>23</sup> also accounts for the increase of adsorption with temperature. It is also to be expected on this theory that adsorption should occur only at the positive plate, since the ferric salt is reduced to the ferrous condition at the negative plate. Ferrous hydroxide is a much stronger base than ferric hydroxide, and the hydrolysis of ferrous sulphate will be negligible compared with that of ferric sulphate; no adsorption should therefore occur at the negative plate.

Adsorption of the hydrolysed ferric iron will take place at the liquid-solid interfaces formed by the lead peroxide and the lead sulphate with the electrolyte. The variation in the electrolyte iron concentration on charge and discharge can be ascribed to the changes in acid concentration which occur during these processes. On discharge the acid concentration in a cell falls, leading to increased hydrolysis of the ferric sulphate and hence to increased adsorption at the positive plate. A drop in the electrolyte iron concentration therefore occurs. The process is probably more complex than this, since the acid in the pores of the plate on discharge becomes very dilute, and is subsequently restored by diffusion, but the resultant effect will be that stated. On charge a very high acid concentration is produced in the pores of the plate by the reaction,



while in addition the iron is migrating away from this plate. This high acid concentration reduces the hydrolysis of the ferric salt and hence the adsorption, and a rise in the solution iron concentration will occur. On standing some time the concentration of acid in the plate pores is reduced by diffusion to that of the main bulk of the solution, the hydrolysis of the ferric sulphate in the plate pores is increased and adsorption occurs, leading to a drop in the solution iron concentration. The value reached will still be higher than in the discharged cell by an amount depending on the difference between the acid concentrations of the cell in the charged and discharged states. The anomalous behaviour observed at 32° is more difficult to explain, but other factors, such as the change in surface area of the solid paste on charge and discharge probably enter into the equilibrium conditions and may, together with the solution volume change on charge and discharge, approximately balance the variations due to the alteration in acid concentration.

The desorption experiments have shown that for charged cells the adsorption is irreversible both with respect to decrease of temperature and to decreasing electrolyte iron content, though not completely so in the latter case. Discharged cells, however, show considerable desorption when out of equilibrium with their solution. It has been shown by Malfitano and Michel<sup>24</sup> that the hydrolysis of ferric chloride is irreversible with respect to temperature, *i.e.*, the fraction hydrolysed does not decrease when the temperature is lowered. This irreversibility diminishes as the acid concentration of the solution is increased and finally vanishes. Even if it be assumed that the hydrolysis of ferric sulphate exhibits an analogous irreversibility, it is improbable that in acid solutions of about 7*N* any such irreversibility

<sup>23</sup> No data for ferric sulphate are available, but the hydrolysis of ferric chloride increases rapidly with temperature when the hydrolysis is small (Landolt Börnstein, *Physik. Chem. Tabellen.*, 1923, 1168).

occurs. In addition, the irreversibility of the adsorption on reducing the electrolyte iron concentration by acid change at constant temperature is not explained.

The irreversibility of the adsorption by the lead peroxide may be attributed to some form of combination between the acidic lead peroxide and the weakly basic ferric hydroxide complex, this irreversible process following the reversible adsorption. No such specific chemical factors are involved in the adsorption by the lead sulphate and this will be reversible. The desorption on electrical working is then attributable to the tendency of the positive plate to send off positively charged ions during charge, thus breaking up the lead peroxide-ferric iron compound and sending the complex ferric hydroxide ion into solution. On discharge the lead peroxide-ferric iron compound is broken up by the passage of the lead peroxide into lead sulphate and, the adsorption of iron by the latter being reversible, a redistribution to the equilibrium state will occur. This theory appears to cover, in a satisfactory manner, the main facts observed. The desorption which occurred with discharged cells on temperature drop, and without working, was greater than the drop on subsequent working, which seems disproportionate, since a discharged plate contains about 25 per cent. lead sulphate and 75 per cent. lead peroxide. This result appears anomalous, but the differences which were being observed were very small.

#### Permanent Loss and Adsorption.

The relation between these two effects may now be seen. The permanent loss and the electrolyte iron concentration show a linear relation (Figs. 1, 2 and 3, Part I.) except for iron concentrations of less than 0.02 g./100 c.c. The form of the curve here is in doubt owing to the difficulty of measuring small permanent losses with any degree of accuracy. Similarly the percentage adsorption and the electrolyte iron concentration are connected by an approximately linear relation (Fig. 2, Part II.) for electrolyte iron concentrations greater than 0.02 g./100 c.c., whereas at lower concentrations there is a marked deviation from this linear relation. Hence over the range for which experimental values of permanent loss and adsorption are available an approximately linear relation holds between them at a given temperature and, from the form of the curves, it is probable that this relation extends to the lowest iron concentrations. It may be noted that since the pure cells contained a small amount of iron some permanent loss must have occurred in these. For an electrolyte iron concentration of 0.001 g./100 c.c., it has been found, by extrapolation to zero iron concentration of the adsorbed iron—permanent loss curves, that a permanent loss of about 1.8 per cent. at 48.9° and about 0.9 per cent. at 18° occurs, at the 4.5 hour rate.

The permanent loss has been found to be recovered to a large extent on the first discharge after acid change and entirely on the second discharge. A cell containing 0.91 g. iron/100 c.c. electrolyte which exhibited a permanent loss of about 33 per cent. had its acid changed twice, with a short intermediate charge to ensure mixing of the electrolyte, and was subsequently discharged. This permanent loss was then almost entirely recovered. Other cells containing 0.1 g. iron/100 c.c. electrolyte have been found after one acid change, with no intermediate charge, to exhibit a similar capacity recovery. *The permanent loss is therefore recoverable by removing the iron.*

### Permanent Loss. Discussion.

The permanent loss cannot be explained by any self-discharge effect during the period of discharge. Even if all the iron in solution were in the ferrous state and reached the positive plate during the discharge period, the self-discharge so caused would only be a small fraction of the observed permanent loss. It must also be noted that, although the adsorption of iron by the lead peroxide is mainly irreversible, the permanent loss is almost completely recovered on the first discharge after electrolyte change. It appears therefore that the lead peroxide molecules to which the adsorbed iron is attached are capable of reacting, otherwise the desorption on discharge is difficult to explain, but that the presence of this adsorbed iron hinders the reaction of other lead peroxide molecules. Any theory must also explain the decrease in the percentage permanent loss as the discharge rate is increased.

It appeared possible that changes in surface tension due to the presence of iron in the electrolyte might alter the volume of the gas trapped in the capillaries of a plate after charging and, hence, change the area of contact between paste and electrolyte. Such an effect would produce a change in the capacity of the cell. The addition of 0.187 g. of ferric iron per 100 c.c. of sulphuric acid of S.G. 1.22 raises the surface tension at an air interface by about 3 per cent. As iron causes a loss in capacity, any agent which lowers this surface tension might be expected to produce a gain in capacity.

Solutions of 1.22 S.G. sulphuric acid were allowed to stand in contact with thymol and menthol respectively for 24 hours,<sup>24</sup> the surface tension at an air interface being thereby reduced by about 20 per cent. and 36 per cent. respectively. The effect of using such acid in lead cells of known capacity was tested, but no increase in capacity was observed. It may be concluded that the surface tension changes do not in themselves afford an explanation of the permanent loss.

Some experiments on the relative wetting powers of solutions of sulphuric acid and ferric sulphate have been carried out. If finely divided lead peroxide be shaken up with toluene and water the solid collects in the toluene layer or at the toluene-water interface, showing that the interfacial tension of toluene against lead peroxide is less than that of water. If for water be substituted a 1.28 S.G. sulphuric acid solution, or a ferric sulphate solution (0.87 g. iron/100 c.c.), the lead-peroxide passes into the aqueous layer. The presence of these electrolytes thus reduces the solid-water interfacial tension, as is to be anticipated since they raise the air-liquid tension.<sup>25</sup> The transition point, where the addition of more electrolyte causes the lead peroxide to move from the toluene to the aqueous layer, has been determined by shaking up varying strength solutions and observing the distribution. The method only permits of a very rough estimation, but using the same sample of lead peroxide throughout the values should be comparable. This transition point occurred at about 0.0075 g. mols./litre for sulphuric acid and at 0.00022 g. mols./litre for ferric sulphate.

A lead peroxide surface will therefore normally hold an adsorbed layer of sulphuric acid when immersed in a sulphuric acid solution, but since ferric sulphate reduces this solid-water interfacial tension much more than sulphuric acid, the ferric iron will be preferentially adsorbed. Hence on

<sup>24</sup> Cf. Edwards, *J. Chem. Soc.*, 127, 744, 1925.

<sup>25</sup> Cf. Porter, *Trans. Far. Soc.*, 17, 394 (1921-22).

the addition of ferric sulphate some of the adsorbed sulphuric acid will be replaced by ferric iron in the form of the complex hydrolysis product. It is probable that the cause of the permanent loss is to be found in this partial replacement of the adsorbed sulphuric acid by the ferric complex. It would appear, however, that any decrease in conductivity due to this cause, across the liquid-solid interface sufficient to account for the permanent loss should appear as an increased internal resistance in the cell, which has not been found (see Part I.). An increased polarisation on discharge due to decreased porosity would occur if this iron complex blocks a capillary, either partially or completely, by being held to the solid surface. Such an effect would only appear in capillaries of the order of a few molecular diameters in width, but since the hydrolysed ferric complex is probably of colloidal dimensions the capillary range is not unduly restricted. All the solid lead peroxide which reacts on discharge is not initially in contact with sufficient acid for the discharge it gives. The lead peroxide may be assumed normally to react with its adsorbed sulphuric acid layer; the water produced by the reaction will not be held by the surface but be replaced by more sulphuric acid since the latter lowers the water-solid interfacial tension. The sulphuric acid supply is partially maintained by diffusion and the reaction proceeds until the concentration polarisation becomes so large that the effective discharge comes to an end. If the supply of acid to any capillary is hindered a decrease in capacity must result. This theory explains satisfactorily the decrease in permanent loss with increase in discharge rate. At low rates considerable action takes place in the smaller capillaries, as is shown by the increased percentage of lead peroxide reacting, but as the discharge rate increases, the depth of working in the capillaries decreases, owing to the lessened time for the necessary diffusion of acid into them to replace that which has reacted. The capacity loss produced by the adsorbed iron will be greater the smaller the capillary and, hence, will be recorded on discharge at low rates, but when, at high discharge rates, the capacity obtained from such capillaries is in any case small, the losses occurring will become less.

In general any non-reacting substance which is adsorbed preferentially to sulphuric acid at the lead peroxide surface may be expected to produce a permanent loss if this adsorbed substance is of large molecular dimensions. The addition of salts such as alkali sulphates would not be expected to lead to any permanent loss since these are of small molecular dimensions and are probably not adsorbed preferentially to sulphuric acid. This was confirmed for sodium sulphate by the toluene-water distribution of lead peroxide, the transition point being found to occur at about 0.1 g. mol./litre. This theory, if confirmed by further work, would throw considerable light on the action of many impurities in the lead accumulator.

### Summary.

1. The relations between the permanent loss occurring in a cell containing iron and the adsorption of iron by the positive paste have been studied.
2. The permanent loss has been measured for a series of temperatures, iron concentrations, and discharge rates.
3. The adsorption of iron by the positive paste increases with decreasing acid concentration and also with increase of temperature. This adsorption has been attributed to the presence of a hydrolysis product of ferric

sulphate. The adsorption by the lead peroxide is to a large extent irreversible, but desorption is produced by the electrical working of cells in which the paste and electrolyte iron concentrations are not in equilibrium.

4. The permanent loss and the adsorbed iron concentration are connected by an approximately linear relation. The permanent loss is recovered by the renewal of electrolyte in proportion as the iron concentration is reduced.

5. Both sulphuric acid and ferric sulphate are adsorbed by lead peroxide, but the latter is adsorbed more strongly. The permanent loss has been attributed to this preferential adsorption of the iron and a theory of the action suggested.

The authors desire to acknowledge their indebtedness to the Admiralty and the Department of Scientific and Industrial Research for permission to publish this paper.

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## THE ELECTRICAL CONDUCTIVITY OF VAPOURS AND LIQUID DROPS DURING INCIPIENT COMBUSTION.

*(Investigations made at the Air Ministry Laboratory, Imperial College of Science and Technology and published by permission of the Director of Scientific Research, Air Ministry.)*

By J. A. J. BENNETT, CARNEGIE RESEARCH FELLOW.

*Received 31st March, 1927.*

The problem of the slow beginning of combustion of liquid fuels has up till very recently remained relatively obscure. The chemistry of the subject has been dealt with by Callendar, King, Mardles, Stern and Fowler,<sup>1</sup> in their recent explanation of the cause of detonation in engines using liquid fuel. The object of the present experiments was to study the physical aspect of slow combustion, in the light of the ionic theory of the electrical properties of gases which has been developed and established by Sir J. J. Thomson and others.

By comparing the temperature variation of the rate of chemical action with that of thermionic emission at the surface of metals in the presence of various reacting gases, Brewer<sup>2</sup> has shown that chemical action is in that case intimately related to the physical processes occurring. Whilst the chemical action immediately preceding detonation in an engine cylinder has now been explained,<sup>1</sup> it is possible that as in the above case the mechanism of the action may be explained on the ionic theory. The following experiments were prosecuted to lead the way to such an explanation. Callendar's nuclear theory of detonation<sup>3</sup> led the writer to investigate the electrical conductivity of liquid drops.

<sup>1</sup> *Engineering*, Feb. 4th, 11th, 18th, 1927.

<sup>2</sup> *Proc. Nat. Acad. Sc.*, September, 1926.

<sup>3</sup> *Aero. Res. Comm.*, R. & M., 1013, 1925.

## Description of Apparatus.

The method of producing slow oxidation of gaseous mixtures was similar to that used by Mardles,<sup>1</sup> a brief description of which will be given. Fig. I. shows the general arrangement. Air supplied under slight pressure from a ten-gallon drum was dried and freed from carbon dioxide before entering the vaporiser, the rate of flow being adjusted by means of a screw clip. The air was bubbled through the liquid in the vaporiser if a rich mixture of vapour and air were desired, but to obtain a lean mixture the air was merely passed over the surface as in the figure. By raising or lowering the vaporiser relatively to the tube which in the case of a rich mixture dips into the liquid, various mixture strengths could be obtained. The mixture of air and vapour was passed through a combustion tube, the temperature of which could be adjusted by means of a Gallenkamp electric furnace with resistance control.

The combustion tubes varied from 2 ft. 6 ins. to 6 ins. in length, the diameter varied from 30 mm. to 15 mm. and both quartz and glass tubes were used. For comparative purposes tubes 15 ins. long and 15 mm. in diameter

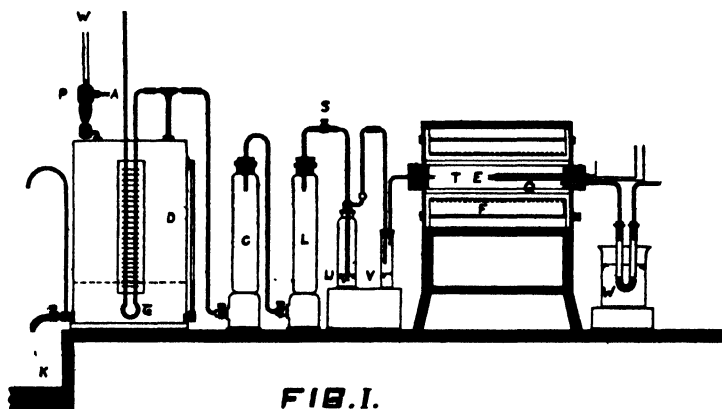


FIG. I.

A, Air inlet. C, Calcium chloride. D, Ten gallon drum. E, Platinum or gold electrodes and platinum-rhodium thermocouple. F, Electric furnace with resistance control. L, Soda lime. P, Filter pump. Q, Quartz tubes. T, Combustion tubes. U, Sulphuric acid. V, Vaporiser.

were used, and since the electrical conductivity of the gaseous mixtures was found not to depend on the material of the tube, the tubes were of glass, except for high temperatures, when quartz tubes were used. The pressure in the combustion tube was atmospheric approximately, since only a slight increase of pressure was necessary to maintain the flow of the mixtures.

Two electrodes, originally made of platinum and later replaced by gold, were made of thick foil and were  $\frac{1}{2}$  cm. square. They were fused and soldered in the case of platinum and gold respectively to wires  $\frac{1}{2}$  mm. in diameter. Two wires, one made of platinum and the other of platinum-rhodium, had their junction at the anode; the wire connected to the cathode was of platinum. Surrounded by quartz tubes of small bore fused together lengthwise, these wires were kept insulated from the gaseous mixtures. The electrodes were thus rigidly placed nearly a centimetre apart.

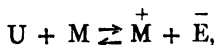
The temperature was measured by connecting the wires from the anode to a millivoltmeter supplied by the Cambridge Scientific Instrument Company. The electrodes being kept at a constant potential difference of 30

volts by means of a battery of small cells, the current passing between the electrodes was measured by a galvanometer of the Lord Kelvin type.

In the experiments with liquid drops air supplied by a compressed air cylinder passed through a sprayer mechanically similar to that used by the writer in experiments with salt vapours in flames.<sup>4</sup> The mixture of air and spray entered the combustion tube where the air and vapour mixture entered in the experiments with vapours.

### Ionisation in Gaseous Media.

The neutral atoms ( $M$ ) are dissociated into ions ( $M^+$ ) and electrons ( $E^-$ ) according to the equation



where  $U$  is the quantity of energy absorbed in dissociation.

Since the mobility of the electrons is of a higher order than that of the ions the conductivity of the medium depends mainly on the number of free electrons present. Ionisation in gases at normal temperatures is of a low order of magnitude and can only be measured by very delicate apparatus.

The apparatus described above was sufficiently sensitive to measure the electrical conductivity of an ordinary Bunsen flame with less than 1 per cent. of error. The degree of ionisation in a salt-free Bunsen flame was taken as the standard relatively to which ionisation in the media could be described as of a low or high order of magnitude. Thus, ionisation in flames containing alkali salt vapours is of a high order of magnitude.<sup>5</sup>

### The Electrical Conductivity of Vapours during Incipient Combustion.

Lean mixtures with air of pure ether, normal hexane, phenol, aniline, iodine, toluidine, and combinations of these, were successively passed through the combustion tube and the temperature in each case slowly raised to the point of inflammation or explosion. At first no displacement of the galvanometer was observed, but after the mixture had passed through the tube for a short time a current was obtained. On dismantling the apparatus it was discovered that the measured conductivity was due to deposits on the electrodes. Consequently, the combustion tube and electrodes were carefully cleaned after each experiment and the temperature was raised as quickly as possible so that the electrical arrangements should not be fouled. In every case the ionisation was found to be of a low order of magnitude, no deflection of the galvanometer being obtained.

The mixture strengths were then increased until it was found that with rich mixtures of the less volatile substances ionisation was quite pronounced above 400° C. Before any displacement of the galvanometer was observed, however, a thick fog appeared in the combustion tube. Not until such a fog was formed was the medium measurably electrically conductive.

At this stage it seemed quite definite that ionisation in vapours during slow combustion was of a low order of magnitude and the results were summed up by Callendar<sup>1</sup> thus: "No trace of ionisation could be detected until the temperature was raised to the point of inflammation, when the intense ionisation which always accompanies flame was immediately apparent."

<sup>4</sup> *Phil. Mag.*, Vol. III., p. 128, 1927.

<sup>5</sup> H. A. Wilson, *Phil. Trans. A*, p. 63, 1915.

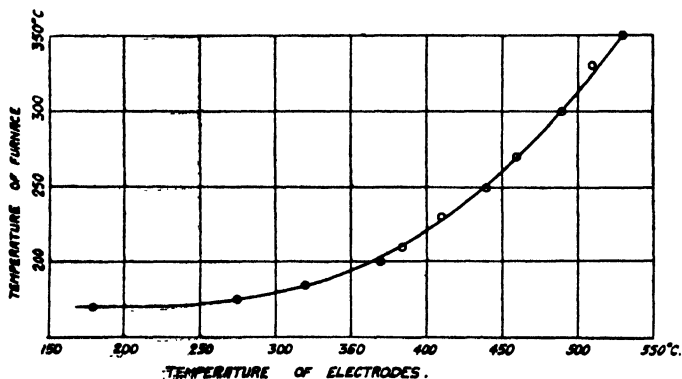
Subsequently, mixtures of hydrogen and acetylene with air appeared to be exceptions to this rule, but it was discovered that the conductivity obtained in these later experiments was due to leakage between the electrodes owing to the accumulation of various substances in the quartz tubes of small bore surrounding the wires leading to the electrodes. When the quartz tubes used in previous experiments had been removed and new ones substituted no conductivity was obtained in rich or lean mixtures of hydrogen-air and acetylene-air. These experiments show that unless total insulation of the electrodes is ensured misleading results may be obtained.

It is also important to make the time of each experiment as short as possible in order to prevent the electrodes from becoming fouled. As an example of the way a small deposit on the electrodes and supporting quartz tubes affects the results, an experiment with hexane-air will be cited. Whilst with a fairly rich mixture of hexane-air with tubes and electrodes completely free from foulness no current could be obtained up to  $600^{\circ}\text{C}$ ., with tubes and electrodes which had become fouled through the time taken to make the experiment at  $500^{\circ}\text{C}$ ., the displacement on the galvanometer scale was 180, the indicator of the Ayrtton shunt being at 300.

### Surface Combustion with Platinum Electrodes.

That the presence of platinum had a marked effect on the combustion of the substances in the combustion tube was not at all obvious if the temperature of the tube were taken to be that measured by the platinum-rhodium thermocouple. It was the discovery of this so-called catalysis which led the writer to substitute gold electrodes for the platinum ones. With gold electrodes no surface action was apparent.

The temperature of the middle part of the furnace was measured by a Callendar platinum thermometer reading on a Whipple indicator. On



**FIG. II.**

heating the furnace, combustion of the hydrogen-air mixture was observed by the formation of water in the U-tube after the mixture had passed through the combustion tube. The hydrogen was supplied by a cylinder of compressed hydrogen and, after gently bubbling through concentrated sulphuric acid, joined the flow of air from the ten-gallon drum before entering the combustion tube.

The temperature of the furnace as measured by the Callendar platinum thermometer and the temperature of the electrodes as measured by the

platinum-rhodium thermocouple were exactly the same until combustion commenced, when the temperature of the electrodes rose rapidly but that of the furnace continued increasing slowly at its former rate. Fig. II. shows the variation of the temperature of the furnace with that of the electrodes for a 50 per cent. mixture of hydrogen-air. The chemical catalytic action of platinum seems therefore to be due to surface combustion.

### The Electrical Conductivity of Liquid Drops-Air Systems During Incipient Combustion.

The only modification in the apparatus used in the preceding experiments in order to measure the electrical conductivity of liquid drops was that already mentioned. Since rich mixtures of vapour were previously

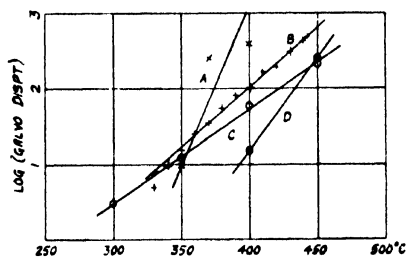


FIG. III.

*Undecane and Miscellaneous Antiknockers—*

- A Undecane plus trace of iron carbonyl.
- B " " saturated solution of iodine.
- C " " " 10 % carbon-disulphide.
- D " " " 10 % carbon-disulphide.

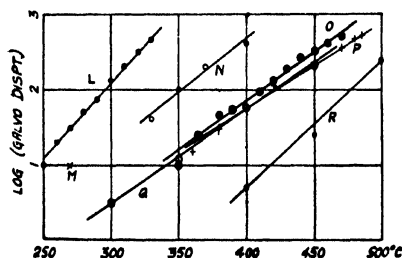


FIG. V.

*Undecane and aromatic bases and phenols—*

- L Cresol.
- M Undecane plus 5 % aniline.
- N " " " phenol.
- O " " " 10 % xylydine.
- P " " " 10 % toluidine.
- Q " " " 10 % toluidine.
- R " " " 10 % toluidine.

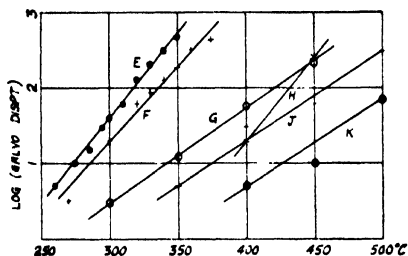


FIG. IV.

*Undecane and Nitrogen Compounds—*

- E Nitrobenzene.
- F Nitroxylol.
- G Undecane.
- H " plus 10 % phenylhydrazine.
- J " " " nitroxylol.
- K " " " nitrobenzene.

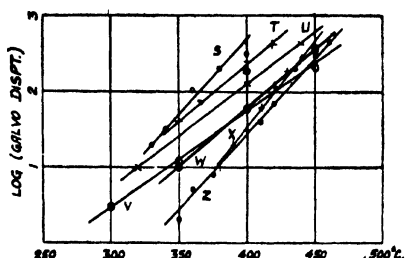


FIG. VI.

*Undecane and Alcohols—*

- S Benzyl alcohol.
- T Undecane plus 10 % ethyl alcohol.
- U " " " benzyl alcohol.
- V " " " benzyl alcohol.
- W " " " amyl alcohol.
- X Ethyl alcohol.
- Z Amyl alcohol.

found to be measurably conductive after fog formation it was expected that liquid drops should have the same order of conductivity. This was found to be so; about 300° C. there was a sufficient number of free electrons in the vapour surrounding the drops to cause a measurable current to flow

between the electrodes. The temperature of each substance was raised gradually from 300° C. to 500° C. Throughout this range the conductivity increased exponentially with the temperature for each substance. With the tremendous increase of free electrons, the drops must become positively charged to a high degree, but, since they move very slowly relatively to the electrons, the current is due almost entirely to the movement of the free electrons.

Figures III., IV., V. and VI. give the experimental results for liquid drops of undecane (b.p. range 198-208° C.) and undecane mixed with various organic substances. Experiments with different mixtures of undecane and toluidine were carried out, but no relationship could be obtained between mixture strength and conductivity, though for each mixture strength the conductivity increased exponentially with the temperature as in the above experiments.

### **Influence of Ultra-Violet Radiation.**

The combustion tube, made of quartz, was surrounded by a coil of nichrome wire which was used instead of the furnace to heat the tube. Another quartz tube of similar dimensions was placed side by side with its axis at a distance of two centimetres from the axis of the combustion tube. This second quartz tube formed part of a mercury arc lamp supplied by the Hewittic Electric Company Ltd., and was filled with luminous mercury vapour rich in ultra-violet light.

It was found that although the action of the light lowered the temperature of initial combustion, it did not supply enough energy to cause measurable ionisation in the case of the combustion of vapours nor did it raise the conductivity of the liquid drops systems to an appreciable extent. At first it was thought to induce considerable ionisation after exposure, but further experiments showed that during the time of exposure deposits had been formed on the electrodes. The increase of ionisation was due to the fouling of the electrodes only.

### **Discussion of Results.**

The main conclusions from these experiments are that the slow combustion of a disperse system of liquid drops of various organic substances in air is accompanied by profuse liberation of electrons and that in mixtures of vapours and air comparatively few electrons are present. The importance of these conclusions with regard to internal combustion engines will now be indicated.

It is well known that liquid drops persist in an engine cylinder at temperatures far higher than are required for their evaporation. This effect is due to the increase of pressure necessarily accompanying increase of temperature. A review of this subject has been given by Callendar.<sup>1</sup>

Consider one particular volume of the engine cylinder. Suppose the temperature of this volume to be suddenly increased relatively to that of the rest of the cylinder. The liquid drops which exist in this particular volume will evaporate and the substance of which the drops were composed will now exist in the molecular state. The electrons will recombine with most of the positive ions into which the drops have been divided, and consequently the quantity *U* in page 297 liberated will be very large.

The fact that ignition occurs at a lower temperature in mixtures of gaseous fuels containing liquid drops than in a completely vaporised

mixture may be accounted for by this supply of energy from the recombination of the electrons and ions. "Detonation," says Callendar,<sup>1</sup> "requires the simultaneous ignition of a considerable proportion of the mixture by something uniformly distributed through the mixture itself." It is probable that such ignition may be started in detonation of the nuclear type by the source of self-ignition explained by the present experiments.

The above work forms part of an investigation on the cause and prevention of detonation in the internal combustion engine carried out at the Air Ministry Laboratory, Imperial College of Science and Technology, London. It was prosecuted under the supervision of Professor H. L. Callendar, C.B.E., LL.D., F.R.S., and with the help of Dr. E. W. J. Mardles, F.I.C., to both of whom the author is deeply indebted.

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## THE DECOMPOSITION OF SOME ORGANIC SUBSTANCES BY THE ELECTRIC SPARK.

By N. R. FOWLER and E. W. J. MARDLES.

*Investigations made at the Air Ministry Laboratory, Imperial College of Science and Technology, and published by permission of the Director of Scientific Research, Air Ministry.*

(Received 31st March, 1927.)

The passage of an electric spark through an organic substance, such as hexane, alcohol, or aniline, is accompanied by considerable decomposition, bubbles of inflammable gases and free carbon separating at the zone of the electric discharge.

Svedberg<sup>1</sup> has shown that the spectrum of the unprotected electric arc between silver electrodes immersed in ethyl alcohol contains not only the silver lines but also the broad carbon bands.

A carbon sol can be readily obtained in an organic medium by passing a succession of electric sparks through it with the use of carbon or iron electrodes. Thus, with the electric discharge from a 10 inch induction coil and Wehnelt interrupter, using iron electrodes, petrol immediately blackened and by filtering or decanting from the separated carbon a yellow liquid, which exhibited the Tyndall effect in a beam of light, was obtained.

The heating effect of the spark on the bulk of the medium was small so that a run of about an hour could be made with a litre of material without external cooling.

Experiments were conducted with a number of substances in order to determine, if possible, the course of the decomposition and whether the results would throw any light on the action of aniline, alcohol, etc., in delaying detonation in the internal combustion engine.

### Composition of the Inflammable Gases.

The chief constituents of the inflammable gases were found to be hydrogen and methane with small amounts of acetylene. When nitrogen

<sup>1</sup> T. Svedberg, *Colloid Chemistry*, p. 37.

was present in the molecule hydrogen cyanide was formed and rendered the medium conducting so that after an interval of time the spark discharge ceased.

Berthelot<sup>2</sup> and later A. Pizzarello<sup>3</sup> observed that electric sparks decomposed organic vapours into acetylene, hydrogen, carbon, etc., whilst recently a study of the decomposition of liquid and solid hydrocarbons by the electric arc has been made by A. Contardi<sup>4</sup> to determine whether acetylene could be produced economically from tar and other oils. He obtained with iron or carbon electrodes 50 volts and 40 amperes, a yield of 22 per cent. acetylene in the gas from anthracene oil, the other constituents being methane 50 per cent., hydrogen 23 per cent., and nitrogen 5 per cent.

In the experiments with ethyl alcohol the electric spark caused a vigorous decomposition and the gases produced contained 38 per cent. carbon monoxide, 20 per cent. methane, and 38 per cent. hydrogen. Acetaldehyde vapour was present and a small amount of acetylene but no carbon dioxide was detected. F. G. Muller<sup>5</sup> in a study of the decomposition of ethyl alcohol by an electric arc, 30-35 volts and 25-30 amperes, obtained a gas of a similar composition, *viz.*, carbon monoxide 20-24 per cent., paraffins 20.4 - 6.8 per cent., hydrogen 46-50 per cent., acetylene 7.9-9.9 per cent., ethylene 6.0-9.6 per cent. with traces of diacetylene and a small amount of acetaldehyde 1.5 per cent., whilst Pizzarello<sup>3</sup> by passing a series of electric sparks through vapours in the Torricellian vacuum obtained the same gases from methyl alcohol, ethyl ether and ethyl formate in addition to ethyl alcohol. It is of some interest to note in this connection that Maquenne<sup>6</sup> by means of the silent electric discharge decomposed both methyl and ethyl alcohol and also obtained carbon monoxide, hydrogen, etc.

The chief constituents of the gaseous products of decomposition are the elements hydrogen and nitrogen and compounds of high thermal stability, *viz.* methane, acetylene, cyanogen, and carbon monoxide.

When chlorhydrocarbons are decomposed by the electric arc or Tesla coil chlorine and the stable gas hydrochloric acid are formed in profusion.<sup>7</sup>

### Solid and Liquid Decomposition Products.

The enquiry has been extended to determine whether solid, apart from the formation of finely divided and colloidal carbon, and liquid substances were formed during the decomposition.

A sample of paraffin oil, b.p. above 182° was submitted to the action of the electric spark for about an hour in order to determine whether any lower boiling-point substance had been formed. After the removal of the carbon the oil was examined. There was a slight increase in density and the critical solution with aniline was raised about a degree, but there was no evidence of the formation of low boiling-point liquids from the fractional distillation data. A similar result was obtained by Contardi<sup>4</sup> who examined oils after prolonged exposure to the arc and found little or no difference in the fractionation data.

<sup>2</sup> *Ann. Chim. Phys.* (4) 1873, 30, 431.

<sup>3</sup> *Gazetta*, 15, 233.

<sup>4</sup> *Atti Congresso naz. chim. Ind.*, 1924, 358; *Chem. Abstrs.* *J. Amer. Chem. Soc.*, 1925, 1941.

<sup>5</sup> *Helv. chim. Acta.*, 1925, 8, 821.

<sup>6</sup> *Bull. Soc. Chim.*, 1884, 40, 60.

<sup>7</sup> Urbain and Clair, *Scal. C.R.*, 1919, 168, 887; Tarczyński, *Z. Electrochem.*, 1916, 22, 252.

The experiments were continued with a homogeneous substance such as pure benzene, so that the formation of new substances could be isolated. When benzene, after the sparking, was fractionally distilled there remained in the flask a very small quantity of a thick oil or tar which did not distil below 250°. The molecular weight determined by the lowering in f.p. of benzene was above 250.

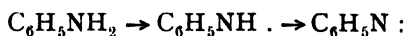
Black tars which decomposed on heating with the formation of dense yellow fumes and a yellow oil were obtained with the aromatic amines, whilst with alcohol in addition to a small amount of acetaldehyde a resinous substance accumulated in the flask. F. G. Muller<sup>5</sup> examined the resin he obtained with the electric arc from alcohol and came to the conclusion that it was the polymerisation product of diacetylene (butadi-inene). It was an insoluble amorphous dark brown solid not melted at 350° but exploding at a red heat.

### The Molecular Disruptive Action of the Spark.

During the passage of the spark through the medium the molecule appears to be broken up not only into the elements, carbon, hydrogen, etc., and stable gases but into free radicles such as  $\cdot\text{CH}$ ,  $\cdot\text{CH}_2$  or  $\cdot\text{CH}_3$  which can only exist momentarily and polymerise or conjugate to form acetylene, etc. The greater the disruptive force the higher the yield of the free elements; the yield of acetylene from hydrocarbons by decomposing with the electric spark of potential difference of the order of 100,000 volts was very much smaller than with the arc of 50 voltage.

The experiment was tried of passing the electric sparks through acetylene. When the current was switched on there was a bright flash in the bulb. It was then found that the spark gap was bridged with threads of carbon which acted as conductors for the current. When these threads were shaken off another bright flash was obtained and carbon deposited across the gap as before. This behaviour could be repeated many times.

With the aromatic compounds the formation of free radicles such as  $\text{C}_6\text{H}_5\cdot$ ,  $\text{C}_6\text{H}_5\text{NH}\cdot$ ,  $\text{C}_6\text{H}_5\text{N}\cdot$ , etc., would result in the formation of complex substances of high molecular weight or tars by their interaction or conjugation. The amount of tar formation was greater with aniline and monomethyl aniline than with dimethyl aniline, whilst the amount of gaseous products was lower. An explanation of this appears to follow from the fact that the primary and secondary amines are capable of yielding free radicles by the direct removal of hydrogen attached to the nitrogen molecule.



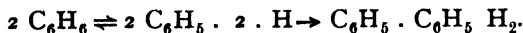
It is of interest to note that tars are produced by the oxidation of the aromatic amines and possibly these are similar in composition to those obtained by the electric spark, since Goldschmidt and Wurzschnitt<sup>6</sup> have shown that the different complex oxidation products of aniline result from the great reactivity of the free radicle  $\text{C}_6\text{H}_5\text{N}\cdot$  and its polymerisation product  $\text{NC}_6\text{H}_5$ :  $\text{C}_6\text{H}_4$ :  $\text{NH}$  produced by oxidation.

The primary and secondary amines have been found to delay detonation in the internal combustion engine, whilst tertiary amines have practically no effect. The behaviour appears to be due to the autoxidation of the  $\cdot\text{NH}_2$  and  $\cdot\text{NH}$  group by organic peroxides formed during slow combustion the radicle  $\text{R}\cdot\text{N}$ : polymerising to form tars.

### Thermal and Electric Decomposition.

There is a close relation between the electric and thermal decomposition. This is seen at once from the composition of coal gas, *e.g.*, hydrogen 50.05, methane 32.87, carbon monoxide 12.39, etc. (Frankland), which are the chief substances present in the inflammable gases obtained during electric decompositions.

Similarly it is well known that benzene vapour at temperatures above 500° C. is converted into hydrogen and substances such as diphenyl, diphenyl benzene, etc.



Maquenne<sup>6</sup> compared the composition of the gases obtained from ethyl alcohol by the silent electric discharge with that by decomposition in tubes heated to redness and found a very close agreement. Recently A. Williams Gardner<sup>9</sup> has studied the thermal decomposition of ethane and has shown that above 550°, hydrogen, methane and small amounts of acetylene, etc., are formed. He regards the mechanism to be due to the formation of  $\cdot \text{CH}_3$  residues from the scission of the C.C bond, whilst at higher temperatures these further dissociate to  $\cdot \text{CH}_2$  and  $\cdot \text{CH}$  which on polymerisation yield ethylene, etc.

### Experimental.

The apparatus consisted of a 10-inch induction coil in conjunction with a Wehnelt electrolytic interrupter, which took the form of a glass jar, 5 inches diameter and 9 inches high, containing a spiral of lead composition tubing as the cathode. A platinum wire, mounted vertically in the jar, as the other electrode could be raised or lowered in the electrolyte (a solution of phosphoric acid 1 : 5). The heat developed in the jar was absorbed by a stream of cold water passing through the lead tubing<sup>10</sup>.

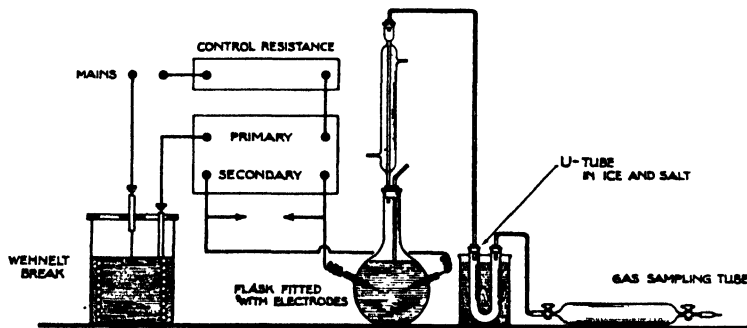


DIAGRAM OF APPARATUS

The current passing through the interrupter and the primary of the induction coil was 8 amperes.

When the platinum wire was just dipping in the electrolyte the discharge from the induction coil appeared as a thin stream of sparks. By lowering the platinum wire the frequency of the discharge was greatly increased and took the form of a hissing flame. This was the type of discharge used for all the experiments. About 200 c.c. of the liquid under

<sup>9</sup> *Fuel*, 1925, 10, 430.

<sup>10</sup> Dewhurst, *Proc. physical Soc.*, 39, 39-77, (1926).

investigation were contained in a glass flask with carbon rods projected through the sides as electrodes. A spark of  $\frac{1}{4}$  to 1 cm. passed beneath the surface of the liquid. Nitrogen was used to displace the air above the liquid in order to avoid ignition of the inflammable gases.

Before collecting the gases they were passed through a freezing mixture in order to condense low boiling-point hydrocarbons. However, none was collected. The residual liquid was fractionated and tested for low and high boiling-point substances.

(1) *Paraffin Oil*. Density 0.82 b.p. 182°-300° C.—When sparks were passed the liquid rapidly blackened due to the separation of carbon, gases were evolved and these were collected and analysed. The carbon was filtered off and the liquid residue in the flask analysed, especially for low boiling-point liquids.

Duration of sparking . . . . .	1 hour.
Average rate of carbon deposit . . . . .	0.0035 g./min.
" " evolution of gas . . . . .	200 c.c./min.
Composition of gas . . . . .	Hydrogen, 35 per cent.
(Average of 10 samples) . . . . .	Methane, 60 per cent.; acetylene and other unsaturated hydrocarbons, 5 per cent.

Distillation range of residual liquid:—

	1st Drop.	5.	10.	20.	40.	60.	80.	90 Per Cent.
Residual liquid . . . . .	179	212	218	223	230	242	258	272° C.
Paraffin oil . . . . .	182	212	217	222	230	243	259	272° C.

The high boiling-point of the paraffin oil rendered it difficult to isolate any new high molecular weight compounds. A slight increase in density and increase in critical solution temperature with aniline indicated the formation of high boiling-point liquids.

(2) *Benzene (Pure crystallisable)*.—This behaves similarly to paraffin oil but with a much greater carbon deposit.

Average rate of carbon deposit . . . . .	0.11 g./min.
" " of evolution of gas . . . . .	200 c.c./min.
Composition of gas . . . . .	Hydrogen, 44 per cent.; methane, 53 per cent.; acetylene and other unsaturated hydrocarbons, 3 per cent.

Distillation of the residual liquid left a small quantity of a thick yellow liquid, b.p. above 250° C. and solidifying point below - 6° C. The molecular weight of this liquid by the freezing-point depression method in benzene was approximately 300.

(3) *Aniline*.—After passing sparks through aniline for approximately 4 minutes, the discharge ceased. The liquid rapidly became hot indicating that its electrical resistance had fallen, the electric current being conducted as through a wire resistance causing heating without disruption. By redistilling the aniline and removing the hydrocyanogen it could once more be used for the sparking experiment for a short period before the same phenomenon was repeated. Gas was evolved, but at a much slower rate than from paraffin oil. Carbon also separated out.

Average rate of carbon deposit . . . . .	0.019 g./min.
" " of evolution of gas . . . . .	70 c.c./min.
Composition of gas . . . . .	Hydrogen, 60 per cent.; methane, 37 per cent.; acetylene, etc., 3 per cent.; hydrocyanogen—small amount; ammonia—not found to be present.

Fractional distillation of the residual liquid left a thick tar. On strongly heating this yielded a few drops of a thick yellow oil.

(4) *Dimethyl Aniline*.—This was found to behave in a similar manner to aniline.

Average rate of evolution . . . 200 c.c./min.  
 Composition of gas . . . Hydrogen, 50 per cent.; methane, 40 per cent.; acetylene, etc., 3 per cent.; hydrocyanogen—small amount.

The residual liquid contained thick tars but in considerably smaller quantities than that obtained from aniline. The rate of gas obtained is approximately three times that given off from aniline.

(5) *Monomethyl Aniline*.—It was found possible to pass a discharge through monomethyl aniline for a slightly longer period than through aniline. But the heating effect was again observed when the discharge ceased.

Average rate of evolution of gas . . . 50 c.c./min.  
 Composition of gas . . . Hydrogen, 70 per cent.; methane, 20 per cent.; acetylene, etc., 5 per cent.; hydrocyanogen—traces.

Distillation of the residual liquid yielded a thick oil, which on strong heating decomposed giving dense yellow fumes.

(6) *Ethyl Alcohol*.—Attempts to pass a discharge through absolute alcohol were not successful. The current merely served to heat the liquid, no disruption taking place. It was found possible, however, to pass sparks through the vapour alone.

The gases obtained had a distinct smell of acetaldehyde, but a freezing mixture failed to condense any appreciable quantity. There was a considerable evolution of gas and only a small quantity of carbon deposited.

Rate of evolution of gas . . . 450 c.c./min.  
 Composition of gas . . . Hydrogen, 38 per cent.; methane, 20 per cent.; carbon monoxide, 38 per cent.; acetylene,  $1\frac{1}{2}$  per cent.

No carbon dioxide was present in the gas. Traces of resinous matter and a small amount of carbon were deposited.

(7) *Acetylene*.—The acetylene gas was contained in a glass bulb 5 cm. diameter with copper electrodes sealed in with wax. A spark gap of  $\frac{1}{8}$  inch was used, the current through the primary of the induction coil being reduced to 2 amperes.

When the current was switched on there was immediately a bright flash in the bulb. It was then found that the spark gap was bridged with threads of carbon which prevented further action. When these threads were shaken off another bright flash was obtained and carbon deposited across the gap as before. This could be repeated many times, a bright flash always appearing when the threads were removed and the current switched on.

The addition of a small percentage of air to the acetylene did not affect the results described above. By adding a greater percentage of air, however, an explosion occurred. In this case there was a smaller deposit of carbon.

# IONISATION IN FLAMES OF VARIOUS ORGANIC SUBSTANCES.

*(Investigations made at the Air Ministry Laboratory, Imperial College of Science and Technology, and published by permission of the Director of Scientific Research, Air Ministry.)*

By J. A. J. BENNETT, CARNEGIE RESEARCH FELLOW.

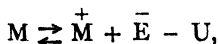
*Received 31st March, 1927.*

The study of the phenomenon of detonation in internal combustion engines has recently given rise to many subsidiary problems of fundamental importance. It has been suggested by many writers that ionisation is one of the chief causes of detonation, though no relation has yet been discovered between the former and the latter. Up till now attention has been devoted mainly to the study of ionisation in gaseous explosions. The object of the present experiments was to determine the correlation, if any, between the degree of ionisation of various substances in flames and the amount of detonation in an engine cylinder charged with fuels containing these substances.

The range of investigation includes an experimental study of ionisation in flames of hexane, ether, alcohol, coal gas, etc., and the effect of adding iron carbonyl, amyl nitrite, etc.,—substances which alter the highest useful compression ratio (H.U.C.R.)<sup>1</sup> of a fuel.

All gases conduct electricity, but very delicate apparatus is required to show that some gases in their natural state possess this property even to a small extent. Unless ions have been produced by raising the temperature, by exposure to active rays, or by some other method, all gases are relatively good insulators.

One of the oldest methods of obtaining gases in an ionised state is by producing flame. Giese,<sup>2</sup> by studying the electrical properties of gases coming from flames, discovered the theory which is now used to explain gaseous conductivity. The current passing between two electrodes at different potentials immersed in gaseous media is at present considered to be due to the movement of the electrons towards the anode and the positive ions towards the cathode. The mobility of the former is of a higher order than the latter, except possibly when the electrons become attached to neutral atoms. At higher temperatures the neutral atoms (M) of gaseous elements dissociate into ions ( $\overset{+}{M}$ ) and electrons ( $\bar{E}$ ) in the following manner:—



where U is the energy absorbed in the process.

<sup>1</sup> The H.U.C.R. is the highest compression ratio which it is worth while to employ with a given fuel. If the compression ratio is raised above this limit excessive detonation leading to pre-ignition and loss of power is obtained. For full information on this subject reference is made to the Aeronautical Research Committee publication, R. & M. No. 1013, on Dopes and Detonation by Callendar, King, and Sims.

<sup>2</sup> *Wied. Ann.*, 17, 519, 1882.

Saha,<sup>3</sup> assuming that the electron is a monatomic gas of atomic weight  $1/1836$  and the energy  $U$  to be the product of the ionisation potential and the electronic charge, has recently developed a theory of thermal ionisation of gaseous elements at high temperatures which has received confirmation by experiments with salt vapours in flames at particular temperatures by Noyes and Wilson,<sup>4</sup> Barnes,<sup>5</sup> and for variation in temperature by the writer.<sup>6</sup> Garner and Saunders,<sup>7</sup> by using an Einthoven galvanometer for measuring the percentage of ionisation occurring in explosions of hydrogen and oxygen, found that Saha's theory holds approximately for gaseous explosions and therefore that the ionisation is mainly thermal as in flames. The similarity between the origin of ionisation in flames and explosions suggests that the present experiments may throw light or shadow on the views expressed by other writers on the relation between ionization and detonation, concerning which there is much diversity of opinion.

### Measurement of Ionisation.

Since the mobility of the electrons is so great compared with that of the positive ions, the current passing between two electrodes immersed in the excited flame medium is almost solely due to the electricity carried by the electrons. Accordingly, the electrical conductivity is proportional to the number of electrons present, and since the number of electrons is equal to the number of positive ions, the conductivity may be taken as a measure of the ionisation. The specific conductivity at a point in the region between the electrodes depends upon the potential gradient at the point as well as the current per unit area of one of the electrodes, guarded to ensure that the lines of force between the electrodes go straight across. The present experiments were not intended to measure the absolute value of the ionisation, and no measurement of the potential gradient at various points between the electrodes was made; it was therefore unnecessary to have one of the electrodes guarded. Precautions were taken to keep the electrodes at a constant distance apart, to keep their position constant in the flame and to keep the temperature of the flame constant; the area of the electrodes and the difference of potential between the latter remained unchanged. The current under these conditions is practically a measure of the degree of ionisation.

*Description of Apparatus.*—Two platinum electrodes each  $\frac{1}{2}$  centimetre square were placed just over the inner cone of an ordinary bunsen flame. They were made of thick foil and welded to wires  $\frac{1}{2}$  millimetre in thickness. The wire connected to the cathode was made of platinum, but the anode was attached to the junction of two wires, one made of platinum, the other of platinum-rhodium. The temperature of the anode could therefore easily be kept constant, the wires leading to the anode being connected to a millivoltmeter supplied by the Cambridge Scientific Instrument Company. The horizontal distance between the electrodes was a little over a centimetre, and this distance was kept constant by passing the wires through quartz tubes of small bore fused together lengthwise. -

A battery of small cells supplied a constant potential difference of 30 volts between the electrodes and the current passing through the flame medium was measured by a Kelvin galvanometer, the sensitiveness of which

<sup>3</sup> *Phil. Mag.*, **40**, 478, 1920.

<sup>5</sup> *Physical Rev.*, February, 1924.

<sup>7</sup> *Trans. Far. Soc.*, October, 1926.

<sup>4</sup> *Astroph. Jour.*, **57**, 20, 1923.

<sup>6</sup> *Phil. Mag.*, Vol. 3, January, 1927.

could be adjusted by a control steel magnet. The deflection on the galvanometer scale indicated a fairly steady current when the flame was shielded by a chimney.

The effect of various substances on the conductivity of the flame was studied, the method of introducing each substance depending on its volatility. The more volatile substances were mixed with the air before entering the flame; the less volatile substances were burned at the end of a quartz tube introduced at the mouth of the burner. Care must be taken to have the connecting wires well insulated and the electrodes free from deposit.

### The Flame Constituents.

Since the ionisation depends on (a) the nature, and (b) the concentration of the flame constituents, (c) the temperature of the flame, (d) the distance of the electrodes from one another, and (e) the amount of deposit on the electrodes, it was necessary to eliminate all these variables except (a), as far as possible, if the true effect of each substance was to be determined. By examination of the table of results it will be noticed that some substances decrease whilst others increase the conductivity of the flame. The action is not a catalytic one, but the variation of the conductivity of the flame is due to the variation of the concentration of electrons in the flame. The presence of substances of low ionisation potential—which is the potential required to give an electron enough energy to ionise a neutral atom—increases the number of electrons present in the flame and therefore increases the current; substances of high ionisation potential decrease the electron concentration and therefore decrease the current.

The following results with the Bunsen flame and the addition of various substances are typical of results obtained with other flames, as will be pointed out later.

	Substance	Effect on Ionisation.	Effect on Detonation. <sup>a</sup>
Nitrogen Compounds	Aniline	Slightly decreases	Delays
	Methyl-aniline	" "	" "
	Di-methyl-aniline	" "	" slightly
	Benzyl-ethyl-aniline	" increases	" "
	Xylidine	Decreases	" "
	Nitrogen-peroxide	"	Markedly induces
	Ammonia	"	Slightly delays
	Phenyl hydrazine	Little effect	Slightly induces
	Amyl-nitrite <sup>b</sup>	Markedly decreases	Greatly induces
	Picric acid	Greatly increases	Induces
Carbonyls	Iron-carbonyl <sup>10</sup>	Greatly increases	Greatly delays
	Nickel-carbonyl	" "	" "
Organic oxides, etc.	Benzoyl-peroxide	Greatly increases	Greatly induces
	Hydrogen-peroxide	" "	Little effect
	Ether	Cooling effect	Induces
Halogens and Halogen Compounds	Iodine	Greatly increases	Delays
	Bromine	" "	Slightly induces
	Ethylene dibromine	" "	" delays
	Acetylene tetrabromide	Increases	" "
	Chloroform	Greatly increases	Little effect
	Dichlorethylene	" "	Slightly induces

<sup>a</sup> Information obtained from the report on Dopes and Detonation by Callendar, King, and Sims<sup>1</sup> and from experiments made by the staff of the Air Ministry Laboratory.

<sup>b</sup> Dark flame between electrodes only.

<sup>10</sup> Reddish-brown deposit on cathode only.

## 310 IONISATION IN FLAMES OF ORGANIC SUBSTANCES

	Substance.	Effect on Ionisation.	Effect on Detonations.
Aldehydes	Valeraldehyde	Slightly decreases	Slightly delays
	Propylaldehyde	Decreases	Little effect
	Paraldehyde	Slightly decreases	Slightly delays
	Oenanthol	" "	Little effect
	Acetaldehyde	" "	Slightly delays
Miscellaneous	Lead xylol	Greatly increases	Markedly delays.
	Ethyl fluid <sup>11</sup>	" "	Greatly delays
	Carbon-disulphide	Decreases	Delays
	Tin oleate	Greatly increases	Little effect
	Sulphonol	" decreases	Delays
	Water	Cooling effect	"
	Ethyl alcohol	" "	"

**Experiments with Different Flames.**

Various experiments were made to confirm the results tabulated above by using flames other than the ordinary Bunsen. The influence of the various substances on the ionisation in a hexane flame was examined and thereafter the ionisation in flames of the substances themselves was determined.

The method of producing the hexane flame consisted in burning a mixture of air and hexane vapour at the ends of four small quartz tubes which were sealed with sealing-wax to a rubber stopper. A long flame was thus produced and the electrodes were placed in the flame just over the inner cones. The rubber stopper was fitted to a vessel containing cotton wool soaked in hexane through which a stream of air was passed. The air, which was supplied under slight pressure from a ten-gallon drum, was dried and freed from carbondioxide by passing through a tower of granular calcium chloride, then through soda-lime and then by bubbling through concentrated sulphuric acid. The flow of air was adjusted by means of a screw clip.

The cathode became coated with deposit very easily and since the current varies very greatly with the amount of deposit on the cathode it was necessary to make each experiment as quickly as possible. The hexane was doped with each substance in turn and the results obtained were exactly similar to those given in the above table.

To complete the investigation, the hexane vessel was replaced by a weighing bottle containing the substance in liquid form to be examined. The weighing bottle was surrounded by a beaker of water placed on an iron plate which could be heated at will by a Bunsen flame. In this way the less volatile substances were vaporised. The air in some cases bubbled through the liquid and in others merely passed over the surface, the extent of the contact of the air with the liquid being varied to give the mixture strength desired. The amount of liquid used during each experiment was determined by weighing the bottle and contents before and after. In this way the mixture strength used in each case was kept constant. The temperature, of course, was kept constant as before by using the platinum-rhodium thermocouple. Those substances in the foregoing table which could be used in this way gave results which showed that flames of substances which increase or decrease the ionisation of a Bunsen flame possess electrical conductivity to a greater or less degree respectively.

<sup>11</sup> "Ethyl fluid" consists of a mixture of lead-tetra-ethyl and ethylene dibromide in the proportion of 3 grams of the former to 2 grams of the latter.

In addition flames of "B.P." petrol, benzene, pentane, acetone, pseudo-cumol, turpentine, and various mixtures were used; a mixture of two substances was found to give a flame the conductivity of which lies between the separate conductivities of the two substances, *e.g.*, "B.P." petrol and carbondisulphide. The current obtained with "B.P." petrol alone was 0.7 microamp., with CS<sub>2</sub> alone 0.03 microamp., with a mixture containing 25 per cent. CS<sub>2</sub>, and 75 per cent. petrol 0.1 microamp.

### Conclusion.

It is evident from these results that although in many cases knock-inducers increase and anti-knocks decrease the ionisation of flames, this is by no means generally so. Consequently, Wendt and Grimms' theory<sup>12</sup> that the advance of free electrons before the flame front ionises the unburnt gas, thus increasing the rate of flame propagation and causing detonation, does not seem at all possible in the light of the present results. If this theory were correct an increase in the ionisation of the flame would increase the rate of flame propagation and induce detonation. But the carbonyls do not behave in this manner.

Neither does the view of Charch, Mack, and Boord,<sup>13</sup> that there is a direct relationship between the intensity of detonation and ionisation receive confirmation. Certainly for particular substances ionisation will increase with increase of knocking since there is a rise in temperature, but the degree of ionisation is not generally a criterion from which to estimate the intensity of detonation, for the carbonyls become exceedingly ionised in flames and the nitrites remain relatively in the neutral state whereas the former tend to delay, the latter to induce, detonation.

We must therefore conclude that, although ionisation accompanies detonation as it does all flame phenomena, there is no simple relationship between them. Ionisation does not appear to be either a cause or effect of detonation, but mainly a temperature effect.

The above work forms part of an investigation on the cause and prevention of detonation in the internal combustion engine made at the Air Ministry Laboratory, Imperial College of Science and Technology, London. It was prosecuted under the supervision of Professor H. L. Callendar, C.B.E., LL.D., F.R.S., and with the help of Dr. E. W. J. Mardles, F.I.C., to both of whom the author is deeply indebted.

<sup>12</sup> *J. Ind. Eng. Chem.*, 1924, 16, 890.

<sup>13</sup> *Ibid.*, April, 1926.

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## THE LAW OF CAPILLARY FLOW IN THE CASE OF COLLOIDS.

BY PROFESSOR ALFRED W. PORTER, AND P. A. M. RAO.

*Received 12th April, 1927.*

It is well known that Poiseuille's equation for the flow of liquids in a capillary tube is not applicable to the case of sols and suspensions; that is to heterogeneous systems in general. Various arbitrary modifications have been proposed in order to accommodate the equation to the experimental facts. These are not all satisfactory because they are not founded on an

scientific basis and, in some cases, they do not even satisfy the principle of dimensions.

In order to extend our knowledge it is of doubtful use to introduce modifications into Poiseuille's equation itself; we must go further back to the mechanical basis on which that equation depends.

In deriving the equation the viscous force per unit area at any interface is taken as being a constant times the gradient of velocity  $\left(-\frac{dv}{dr}\right)$  at right angles to the surface: the constant being the (coefficient of) viscosity ( $\mu$ ). It is the constancy of  $\mu$  that is in question when we are dealing with heterogeneous media. There is no fundamental reason why it should be a constant. It has been found to be so for simple liquids, but it may not be so in general. Nearly all physical factors (such as thermal conductivity, elastic constants, etc.) are found, in the long run, to be variables. It is apparently insufficient, in general, to take the viscous force per unit area as being a constant  $\times \frac{\partial v}{\partial r}$  and some other more complicated function of the rate of shear must be assumed; for example the constant may be replaced by

$\mu_0 + a \frac{\partial v}{\partial r}$  where  $\mu_0$  and  $a$  are constants; or by such other function as may satisfy experiments.

In order to obtain sets of data obtained as nearly as possible under similar conditions we have made determinations by the capillary tube method of the flow under various pressure-gradients of various sols, in particular sols of starch of three concentrations.

The horizontal capillary tube (about 35 cms. long) was completely immersed in

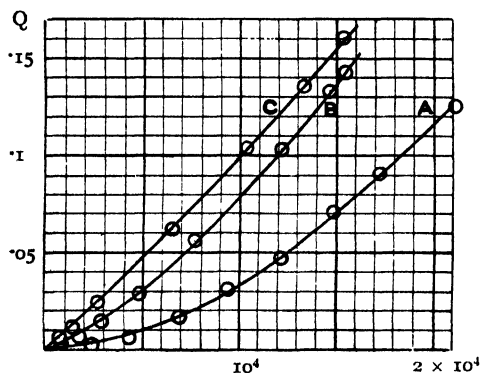


FIG. 1.—Starch sols.  
A 10%, B 8%, C 6%.

a constant temperature tank. The pressure was applied by means of a large gas cylinder in which air was compressed to the pressure required; the value of the pressure was determined by a liquid manometer. The back pressure due to surface tension at the exit of the capillary was eliminated by the exit being made just to touch the surface of the liquid collected; this adjustment could be maintained owing to the collecting vessel being mounted on a 'levelling table,' the length of which was altered throughout the course of an experiment.

The capillary tube was carefully calibrated; the radius given is half the mean of 12 diameters. The liquids used were, in the main, very viscous and therefore it was not thought necessary to introduce any correction for the kinetic energy of flow.

The final data for starch sols are given in the following tables A, B, C. In each case the capillary tube was 37.5 cms. long and of radius 0.0376 cms. The starch (pure soluble starch) was mixed with a small quantity of cold distilled water to form a thick paste. Boiling distilled water was then added until the required dilution was obtained. The sol was finally filtered through a close-textured piece of cloth. An interval of 48 hours was

allowed to elapse before the sol was used in the case of A and 24 hours in the case of B and C.

	Wt. Collected. (Grams).	Time (Seconds).	Q = Volume Time ( $\times 10^3$ ).	Pressure Drop, cm. of Hg.	Pressure Gradient, G, Dynes/cm.
A. Starch Sol., 10 per cent. ( $c=0.1$ ), Temp. $12.3^\circ\text{C}$ ., Density 1.025	1'127	759	1'449	6'74	2,398
	4'21	624'4	6'579	12'47	4,136
	10'35	608'2	16'61	19'65	6,992
	18'94	610'4	30'28	26'46	9,414
	29'66	613'4	47'18	34'17	12,160
	44'57	615'8	70'62	41'89	14,900
	56'49	607'7	90'69	48'84	17,380
	55'38	433'3	124'9	59'50	21,170
B. Starch Sol., 8 per cent. ( $c=0.08$ ), Temp. $15.95^\circ\text{C}$ ., Density 1.007	2'354	716'5	3'264	2'28	813
	6'133	713'0	8'547	5'24	1,854
	10'739	711'4	15'00	8'24	2,932
	21'286	715'4	29'50	13'49	4,798
	40'947	720'8	56'44	21'21	7,546
	55'869	543'6	102'1	33'89	12,060
	57'238	424'1	134'1	41'53	14,780
	53'737	375'2	142'3	43'61	15,520
C. Starch Sol., 6 per cent. ( $c=0.06$ ), Temp. $14.13^\circ\text{C}$ ., Density 1.006	3'86	607'6	6'320	2'15	765
	6'36	603'0	10'49	4'13	1,470
	14'85	605'5	24'39	7'74	2,754
	19'54	425'5	45'66	13'18	4,688
	19'07	303'5	62'48	18'26	6,497
	31'52	304'6	102'9	28'99	10,310
	34'25	251'6	135'4	37'10	13,200
	39'12	242'6	160'3	43'12	15,340

### Interpretation.

To interpret these curves we may assume that the viscosity is a function of the rate of shear-diminishing as that rate increases. The value of the viscosity cannot always be directly determined from the curves of flow. The observed flow ( $Q$ ) is only obtained by a double integration from the original equation in which the dependence of the viscosity upon the rate of shear is expressed and by these integrations the transverse rate of shear is eliminated.

The simplest assumption to make is that the viscosity ( $\mu$ ) varies as an inverse power of the rate of shear  $\left(-\frac{\partial v}{\partial r}\right)$ .

Consider the case of uniform straight-line motion of the fluid in a capillary tube of radius  $R$ . Let  $G$  equal the longitudinal pressure gradient  $\left(-\frac{dp}{dl}\right)$ . Divide up the tube into coaxial cylinders. Select one of radius  $r$ . Then the assumption of uniform flow requires that

$$2\pi r\mu\frac{\partial v}{\partial r} = -\pi r^2 G$$

or

$$-\frac{\partial v}{\partial r} = \frac{Gr}{2\mu}.$$

Let  $\mu = \mu_1\left(-\frac{\partial v}{\partial r}\right)^{-n}$ ; then

$$\left(-\frac{\partial v}{\partial r}\right) = \left(\frac{2\mu_1}{Gr}\right)^{\frac{1}{n-1}} = \left(\frac{Gr}{2\mu_1}\right)^m \quad (\text{say}).$$

whence 
$$v = \left( \frac{G}{2\mu_1} \right)^m \frac{R^{m+1} - r^{m+1}}{m+1}$$

and 
$$Q = \int_0^R 2\pi v r dr = \pi \left( \frac{G}{2\mu_1} \right)^m \frac{R^{m+3}}{m+3}.$$

In this case the dependence of  $Q$  upon the pressure gradient determines  $m$  and consequently  $n$ .

This form is found to satisfy the experimental points very fairly with the following values:—

	$c$	$m$	$n$
A	·1	2	·5
B	·08	1·3	·25
C	·06	1·1	·091.

If further we endeavour to make the curves fit in with the value for pure water we get finally,

$$\mu = \frac{·011 + 6·4[10c]^{12}}{\left[ -\frac{\partial v}{\partial r} \right]^{490c^3}}.$$

These numbers must not be taken to indicate more than the approximate laws of dependence of  $\mu$  upon the concentration.

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## NOTE ON THE SORET EFFECT.

BY PROFESSOR ALFRED W. PORTER.

(Received 12th April, 1927.)

THE gradient of concentration of a solution corresponding to a gradient of temperature (known as the Soret effect) may be explained on the following lines.

Consider an imaginary interface in the solution. Let  $\lambda$  be the mean free path of the solute molecules,  $u_1$  the mean velocity of agitation at a layer a distance  $\lambda$  in front of the interface, and  $u_2$  the mean velocity at a distance  $\lambda$  behind it. If the molecular concentrations at these two layers are  $n_1, n_2$  and if we consider one-sixth of the molecules as moving on the average in any one direction at any time, then the number crossing the interface per unit area per unit time in one direction is  $\frac{n_1 u_1}{6}$  and in the other direction is  $\frac{n_2 u_2}{6}$ . When these are equal the local concentrations remain

unchanged or  $d(nu) = 0$ . But  $u$  is proportional to the square root of the absolute temperature; hence the condition for equilibrium becomes

$$d(nT^{\frac{1}{2}}) = 0.$$

The degree of accuracy with which this simple equation is obeyed is seen by examining the important sets of experimental results obtained by Mr. C. C. Tanner.<sup>1</sup>

<sup>1</sup> *Trans. Farad. Soc.*, 23, 91, 1927.

Take first the case of KCl solutions.

Normality $n$ .	$T_1$ .	$T_2$ .	$\Delta n$ .	$n_1 T_1^{\frac{1}{2}}$ .	$n_2 T_2^{\frac{1}{2}}$ .	$\frac{di}{i}$ .
3.685	48.90	25.00	-.162	64.67	65.03	.0057
2.945	49.00	25.00	-.125	51.74	51.92	.0035
2.210	48.30	24.60	-.089	38.83	38.89	.016
1.472	48.60	24.80	-.057	25.90	25.89	-.00035
.738	48.90	25.20	-.026	12.92	12.97	-.0031

In this table  $n_1 = n - \frac{1}{2}\Delta n$  and  $n_2 = n + \frac{1}{2}\Delta n$ ,  $n$  being the normality when the solution is at uniform temperature.

It is seen that the constancy of  $nT^{\frac{1}{2}}$  is very good. Even the small defect may be allowed for by a factor,  $i$ , depending on the ionisation. We should now expect  $inT^{\frac{1}{2}}$  to be constant or

$$\frac{d(nT^{\frac{1}{2}})}{nT^{\frac{1}{2}}} + \frac{di}{i} = 0.$$

In the last column I have tabulated the values of  $\frac{di}{i}$  calculated from the formula. The proportionate change in  $i$  due to the change in temperature is so small that it is a question whether it does not fall within the range of experimental error: the greatest value due to the drop of 20 degrees being only 7 parts per thousand.

This simplicity does not apply to the values for all substances. For example, for  $H_2SO_4$  the values calculated for  $\frac{di}{i}$  are very considerable.

This mode of examination is safer than that adopted by Mr. Tanner because 20 degrees drop in temperature is too large to be treated as a differential. The gradient of temperature may be practically uniform; it will only differ from uniformity owing to the thermal conductivity varying with the concentration and owing to the escape of heat from the sides of the vessel. On the other hand, the gradient of concentration will not be uniform. If it be assumed that  $T = T_0 + bx$  where  $b$  is the gradient of temperature, and if  $nT^{\frac{1}{2}} = \text{const.} = c$  then

$$n = \frac{c^{\frac{2}{3}}}{(T_0 + bx)^{\frac{1}{3}}}$$

from which the average value of  $n$  is

$$\bar{n} = \frac{2c^{\frac{2}{3}}}{bl} (T_1^{\frac{1}{3}} - T_0^{\frac{1}{3}})$$

and

$$\frac{\Delta n}{\bar{n}} = - \frac{\Delta T}{2[T_1 T_0]^{\frac{1}{2}}}$$

Here  $T_1$  and  $T_0$  are the extreme temperatures. The value of  $\bar{n}$  may be identified with the "normality" of the solution; the values  $\Delta n$  and  $\Delta T$  are the differences of extreme values however great. Hence we see that the values of  $\frac{1}{\bar{n}} \frac{\Delta n}{\Delta T}$  should be inversely proportional to the geometric mean of the extreme temperatures.

The presence of the factor  $i$  and its difference in different cases is probably the cause of the difference of the Soret effect in different cases, for if

$$d(inT^{\frac{1}{2}}) = 0$$

then 
$$\frac{dn}{n} + \frac{1}{2} \frac{dT}{T} + \frac{di}{i} = 0.$$

But if 
$$\frac{di}{i} = -\frac{1}{2} \frac{dT}{T}$$

then 
$$\frac{dn}{n} = 0.$$

This is presumably nearly the case with  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{LiCl}$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{Li}_2\text{SO}_4$ .

It must be added that although  $i$  is a factor introduced to allow for the complications arising from ionisation it may not be simply the van't Hoff constant.

## THE VELOCITY OF THE DECOMPOSITION OF NITROACETIC ACID IN AQUEOUS SOLUTION.<sup>1</sup>

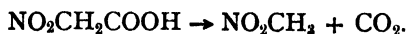
BY KAI JULIUS PEDERSEN.

(Received 31st January, 1927.)

(Communicated by PROFESSOR J. W. MCBAIN.)

The work was undertaken in order to examine the effect of neutral salts and strong acids on the velocity of a chemical reaction, in which a fairly strong undissociated acid takes part, while the ion is inactive. The decomposition of a strong acid  $\text{HX}$  whose ion  $\text{X}^-$  is stable is an example of such a reaction, and it is possible to study the displacement by electrolytes of the equilibrium  $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$ .

Steinkopf and Kirchhoff,<sup>2</sup> who first prepared free nitroacetic acid, have shown that it is stable in strong alkaline solution, while it decomposes in acid solution, according to the equation:



It seems probable, therefore, that the nitroacetate ion is stable while the undissociated nitroacetic acid is unstable.

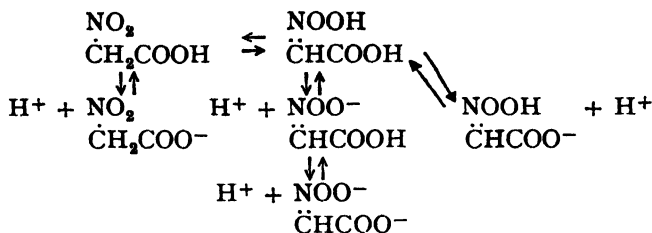
In this work the kinetics of the decomposition of nitroacetic acid in aqueous solution at the temperature  $20.00^\circ$ , have been investigated by measuring the pressure of carbon dioxide above the solution during the reaction by means of the simple apparatus described by Brönsted and King.<sup>3</sup>

<sup>1</sup> Part of a thesis submitted for the degree of Doctor of Philosophy at the University of Bristol in October, 1926.

<sup>2</sup> *Ber.*, 1909, 42, 3925.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1925, 47, 2523.

Nitroacetic acid is a dibasic acid. According to Hantzsch,<sup>4</sup> its dissociation is as follows:



Potassium nitroacetate was prepared from nitromethane by the method of Steinkopf and Kirchhoff.<sup>2</sup> The free nitroacetic acid was prepared from the salt by a slightly different method from that of Steinkopf and Supan.<sup>5</sup> 10 g. of potassium nitroacetate were added in small portions to 50 c.c. of 3 molar hydrochloric acid and 200 c.c. ether in an Erlenmeyer flask cooled in an ice salt mixture. During the addition, the flask was shaken. The aqueous layer was extracted twice with 50 c.c. of ether. These three ethereal solutions were mixed and dried with phosphorous pentoxide and the ether was evaporated in a current of dry air at the temperature 25° to 30°. When only a small volume was left, chloroform was added and the evaporation continued for some time. After cooling in an ice salt mixture, the crystals of nitroacetic acid were sucked from the mother liquor, the yield being 85 per cent. The acid was recrystallised twice from chloroform, and further crystallisation from chloroform did not alter the velocity of the decomposition.

The experiments were of two kinds (a) in solutions containing strong acids, (b) in buffer solutions. The reaction was always found to be monomolecular. In hydrochloric acid, the velocity constant decreased as the concentration of acid increased. A greater velocity constant was found in acetate acetic acid buffer solutions than in hydrochloric acid. This constant,  $k_0 = 0.0316$  (min. <sup>-1</sup>, dekad. logs.), was found to be independent of changes in the hydrogen ion concentration within the range of the acetate buffer solution. Contrary to expectation, the kinetic experiments show that the monovalent ion (or rather one of the three isomeres) is decomposed monomolecularly, while the undissociated acid  $\text{NO}_2\text{CH}_2\text{COOH}$  is stable in aqueous solution.

### Calculation of the Velocity Constants.

The experiments in buffer solutions at constant hydrogen ion concentrations were calculated graphically by means of the simple formula:

$$kt = J + \log P \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $k$  is the velocity constant,  $t$  is the time in minutes,  $J$  is an integration constant, and  $P = p_\infty - p$  is the difference between the pressures at the time  $\infty$  and  $t$ , read off on the mercury manometer. Dekadic logarithms were used.

In the experiments with solutions of strong acids the hydrogen ion concentration decreases a little during the reaction, due to the decomposition of the nitroacetic acid. Therefore the degree of dissociation of the

<sup>4</sup> Ber., 1899, 32, 575.

<sup>5</sup> Ber., 1910, 43, 3249.

### 318 VELOCITY OF DECOMPOSITION OF NITROACETIC ACID

nitroacetic acid increases during the reaction. Otherwise, the reaction would be exactly monomolecular, the constant being  $k = a \cdot k_0$ , as is the case when the concentration of the nitroacetic acid is very small compared with that of the strong acid. It is therefore convenient always to express the results of the acid experiments by calculation of the velocity constant corresponding to a zero concentration of nitroacetic acid and the final concentration of hydrogen ions. This constant can be calculated by means of the following formula :

$$kt = J - \log (P + \Delta),^6 \quad . \quad . \quad . \quad (2)$$

where

$$\Delta = \frac{K \cdot f}{(K + a)^2} \cdot P^2.$$

K is the ordinary "concentration dissociation constant" :

$$K = \frac{c_{H^+} \cdot c_{X^-}}{c_{HX}}$$

K is dependent on the salt concentration.  $a$  is the concentration of strong acid.  $f$  is the constant ratio between the concentration of nitroacetic acid in the solution and P.

It is assumed that  $a$ , the concentration of strong acid, is equal to the hydrogen ion concentration when all the nitroacetic acid is decomposed, the strong acid being completely dissociated. It is also assumed that the change in ionic concentration due to the decomposition of the nitroacetic acid does not affect K sufficiently to have any influence on  $k$ , the slope of the straight line obtained by plotting  $\log (P + \Delta)$  against  $t$ .

From  $k$  it is easy to calculate the concentration dissociation constant K. The degree of dissociation of nitroacetic acid in infinite dilution in the used solution of strong acid is,

$$a = k/k_0 \quad . \quad . \quad . \quad (3)$$

The dissociation constant is

$$K = a \frac{a}{1 - a} \quad . \quad . \quad . \quad (4)$$

As seen from formulae (1) and (2) it is not necessary to notice the exact time when the nitroacetic acid is dissolved in the solution, nor to know the exact weight of the nitroacetic acid. It is sufficient to read off the pressure  $p$  and the time  $t$  several times during the reaction and read off the pressure  $p_\infty$  when all the nitroacetic acid is decomposed. In all the experiments, 100 c.c.s solution and about 0.1 grams of nitroacetic acid were used. Thus the initial concentration of nitroacetic acid was always about 0.01 molar.

<sup>6</sup> Formula (2) can be derived mathematically from the mass action equation and the equation for the velocity of a monomolecular reaction :

$$\frac{x(a + cx)}{1 - x} = K \quad \text{and} \quad -\frac{dc}{dt} = \frac{k_0}{\log e} cx,$$

where  $c$  is the total concentration of nitroacetic acid (dissociated and undissociated) at the time  $t$ ,  $x$  is the degree of dissociation of the nitroacetic acid at the time  $t$ . Neglecting the fourth or greater power of  $\frac{a}{x} - 1$  and of  $\frac{K \cdot c}{(K + a)^2}$ , we get the following formula,

$$k \cdot t = J - \log (P + \Delta) - 0.14 \cdot \left( f \cdot \frac{K \cdot P}{(K + a)^2} \right)^3.$$

The last member is usually too small to have any influence.

The following description of the experimental data is divided into three parts. The first part deals with experiments in strong acids and the dissociation constant of nitroacetic acid, the second part gives the velocity constant for the decomposition of the nitroacetate ion and the third part gives the results of an examination of the effect of various salts on the velocity of the decomposition of the nitroacetate ion.

### The Dissociation Constant of Nitroacetic Acid.

*Solutions of Hydrochloric Acid.*—A series of determinations of the velocity constant for the decomposition of nitroacetic acid in solutions of hydrochloric acid of different concentrations showed a rapid decrease in the velocity when the concentration of strong acid was increased. This can be explained by assuming that only the monovalent ion decomposes, while the undissociated acid is stable or practically so. Using this assumption, it is possible to calculate the concentration dissociation constant  $K$  of the nitroacetic acid (see the formulas (2), (3) and (4)). In the Table I. the results of a series of experiments with hydrochloric acid are given. The first column gives the concentration of the hydrochloric acid, the second column the velocity constant  $k$ , the third column the degree of dissociation of the nitroacetic acid,  $\alpha = k/k_0$ , where  $k_0 = 0.0316$  (see p. 321), and the fourth column the concentration dissociation constant, calculated from formula (4).

$K$  is not quite constant, but increases when the concentration of hydrochloric acid is increased. This is to be expected from the theory of complete dissociation and of interionic forces. For the dissociation of an acid:  $HX \rightleftharpoons H^+ + X^-$ , the thermodynamic mass action law gives:

$$K_a = \frac{a_H a_X}{a_{HX}} = K \cdot \frac{f_H f_X}{f_{HX}},$$

where  $K_a$ , the thermodynamic dissociation constant, is a true constant.  $a_H$ ,  $a_X$ , and  $a_{HX}$  are the activities and  $f_H$ ,  $f_X$ , and  $f_{HX}$  the activity coefficients of  $H^+$ ,  $X^-$  and  $HX$ . In dilute solution we have approximately  $f_{HX} = 1$ , and  $f_H = f_X = f$ . Hence

$$K = K_a \frac{1}{f^2} \text{ or } \log K = \log K_a - 2 \log f \quad (5)$$

Bjerrum<sup>7</sup> suggests the following interpolation formula for the activity coefficients of a monovalent electrolyte:

$$- \log f = k_a \sqrt[3]{c_{ion}},$$

where  $c_{ion}$  is the total concentration of, say, cations and  $k_a$  is the activity constant. Ebert<sup>8</sup> has shown that this cube root formula is in agreement with the formulæ of Debye and Hückel<sup>9</sup> for mono-monovalent electrolytes in concentrations between 0.01 and 0.2 molar.

We shall use this formula on the  $K$ -values calculated from the experiments. The fifth column in Table I. gives the mean value of  $c_{ion}$  during the reaction.  $c_{ion} = c_{HCl} + \frac{\alpha}{2} 0.01$ , the initial concentration of nitroacetic acid being about 0.01 molar in all the experiments.

<sup>7</sup> *Z. Elektrochem.*, 1918, **24**, 321; *Z. anorg. Chem.*, 1920, **109**, 275.

<sup>8</sup> *Z. Elektrochem.*, 1924, **30**, 65.

<sup>9</sup> *Physikal. Z.*, 1923, **24**, 185.

TABLE I.  
THE DECOMPOSITION IN SOLUTIONS OF HCl.

HCl.	$h$ .	$a$	K.	$c_{ion}$ .	$\sqrt[3]{c_{ion}}$ .	$-\log K$ .
0.01002	0.0229	0.725	0.0264	0.0136	0.239	1.578
0.01002	0.0231	0.731	0.0273	0.0137	0.239	1.564
0.01016	0.0232	0.735	0.0282	0.0138	0.240	1.550
0.0200	0.01835	0.581	0.0278	0.0229	0.284	1.556
0.0200	0.0186	0.589	0.0287	0.0229	0.284	1.542
0.0200	0.1874	0.594	0.0292	0.0230	0.284	1.535
0.03006	0.1575	0.499	0.0299	0.0326	0.320	1.524
0.03006	0.0158	0.500	0.0301	0.0326	0.320	1.522
0.0400	0.0136	0.431	0.0304	0.0422	0.348	1.518
0.0400	0.0136	0.431	0.0304	0.0422	0.348	1.518
0.0470	0.0128	0.405	0.0320	0.0490	0.366	1.495
0.0480	0.0126	0.399	0.0318	0.0500	0.368	1.498
0.0500	0.01245	0.394	0.0325	0.0520	0.374	1.488
0.0502	0.01194	0.378	0.0305	0.0521	0.374	1.516
0.0519	0.0121	0.384	0.0322	0.0538	0.377	1.492
0.0600	0.01110	0.352	0.0326	0.0618	0.395	1.487
0.06016	0.01108	0.351	0.0326	0.0620	0.396	1.487
0.0699	0.01014	0.322	0.0332	0.0715	0.415	1.479
0.08022	0.00941	0.298	0.0341	0.0817	0.434	1.467
0.08022	0.00935	0.296	0.0338	0.0817	0.434	1.471
0.0898	0.00867	0.278	0.0346	0.0912	0.450	1.460
0.1000	0.00801	0.254	0.0340	0.1013	0.465	1.469
0.7985	0.00147	0.0465	0.0390	0.799	0.927	1.409

In Fig. 1,  $-\log K$  is plotted against  $\sqrt[3]{c_{ion}}$ . The points fall fairly well on a straight line giving the general formula for the dissociation constant of nitroacetic acid in solutions of hydrochloric acid:

$$-\log K = 1.680 - 0.488 \sqrt[3]{c_{ion}}. \quad (6)$$

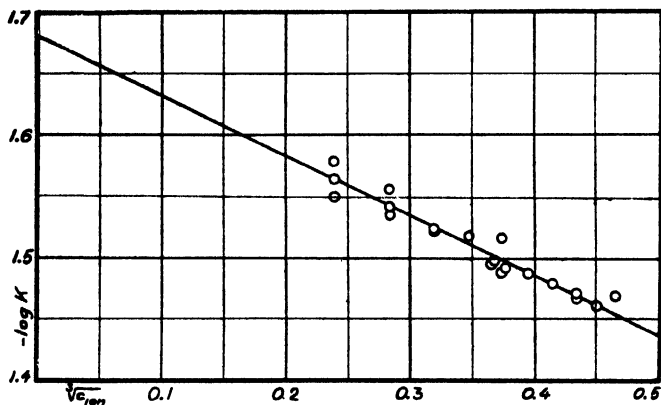


FIG. 1.

By extrapolation to infinite dilution we get  $K_a = 0.021$ . From equations (5) and (6) we get the activity coefficients of the ions of nitroacetic acid in solutions of HCl:

$$-\log f = 0.244 \sqrt[3]{c_{ion}}.$$

Bjerrum finds for KCl<sup>10</sup>

$$-\log f = 0.25 \sqrt[3]{c_{ion}}.$$

<sup>10</sup> *Z. anorg. Chem.*, 1920, 109, 277.

The good agreement justifies the assumption that the undissociated nitroacetic acid is stable compared with the monovalent nitroacetate ion.

**Solutions of HCl + NaCl.**—A further check on the assumption is given by a series of experiments in mixtures of hydrochloric acid and sodium chloride, where the total concentration of ions is kept constant, while the ratio  $\frac{c_{\text{HCl}}}{c_{\text{NaCl}}}$  is varied. The dissociation constant should keep almost constant, because the activity coefficients depend chiefly upon the total concentration of electrolyte, and only to a small extent on the individual nature of the ions. In Table II., the results of three series of experiments where the total concentration of chloride is 0.100, 0.030 and 0.010 *N.* are given. In 0.1 *N.* chloride there is a small variation in *K.* In 0.01 *N.* chloride the individual difference between the hydrogen ion and the sodium ion is without importance.

TABLE II.

THE DECOMPOSITION IN SOLUTIONS OF HCl + NaCl.

$C_{\text{Cl--}}$	HCL.	<i>k.</i>	<i>K.</i>	$C_{\text{Cl--}}$	HCL.	<i>k.</i>	<i>K.</i>
0.100	0.010	0.0248	0.0366	0.030	0.010	0.0236	0.0298
	0.010	0.0247	0.0362		0.0102	0.0238	0.0311
	0.020	0.0204	0.0364		0.020	0.0190	0.0304
	0.020	0.0203	0.0359		0.030	0.01575	0.0299
	0.040	0.0147	0.0349		0.030	0.0158	0.0301
	0.040	0.0148	0.0352	0.010	0.0033	0.028	0.027
	0.050	0.0131	0.0354		0.0067	0.0255	0.028
	0.075	0.0100	0.0347		0.0100	0.0229	0.0264
	0.100	0.00800	0.0338		0.0100	0.0231	0.0273
	0.100	0.00805	0.0341		0.0102	0.0232	0.0282
0.100	0.00801	0.0340					

### The Velocity of Decomposition of the Nitroacetate Ion.

**Experiments in Buffer Solutions.**—Nitroacetic acid is a fairly strong acid. Its dissociation constant is about 0.035 in 0.1 molar mono-monovalent electrolyte and about 0.021 in infinite dilution, when no electrolyte is present. (See above.) In a buffer solution having a  $p_{\text{H}}$  greater than 4, the first dissociation is practically complete. Therefore the decomposition of the monovalent nitroacetate ion can be studied in a buffer solution of a  $p_{\text{H}}$  between 4 and 5. Here the second dissociation is found to play no part, as seen from the constancy of  $k_0$  obtained when  $c_{\text{H}+}$  is varied. For the calculation of the velocity constant in the buffer solutions the simple formula (1) can be used, because there is no change in the degree of dissociation during the reaction.

Most of the experiments were carried out in acetic acid-sodium acetate buffer solutions, a few of them in mixtures of succinic acid and acid sodium succinate.

The reaction is completely monomolecular, and the constant  $k_0$  is independent of the hydrogen ion concentration for  $2 \cdot 10^{-4} > c_{\text{H}+} > 10^{-5}$ .

The mean value of four experiments with succinate buffer solution was  $k_0 = 0.0316$ , and of 34 experiments with acetate buffer solution  $k_0 = 0.0316$ .

**Effect of Salts.**—Various neutral salts were found to have a very specific influence on the decomposition of the nitroacetate ion. The measurements were usually done in a standard buffer solution (S.B.): 0.060 molar acetic

TABLE III.

SOLUTION: S.B. + SODIUM SALTS.

Salt.	$k$ .	Salt.	$k$ .
0.46 M. NaCl	0.0317	0.25 M. $\text{Na}_2\text{SO}_4$	0.0317
0.96 M. NaCl	0.0318	0.50 M. $\text{Na}_2\text{SO}_4$	0.0322
1.00 M. $\text{NaNO}_3$	0.03144	0.25 M. sucrose	0.03185

TABLE IV.

SOLUTION S.B. + LITHIUM CHLORIDE.

$c$ .	$k$ .	$k_0 - k$ .	$(k_0 - k)/c^{2.5}$ .	$(k_0 - k)/c^{0.78}$ .
0.158	0.0312	0.0004	0.04	(0.0017)
0.190	0.0309	0.0007	0.045	(0.0026)
0.237	0.03075	0.00085	0.031	(0.0026)
0.244	0.0305	0.0011	0.038	(0.0033)
0.284	0.0300	0.0016	0.038	(0.0043)
0.316	0.02955	0.00205	0.036	0.0050
0.316	0.02945	0.00215	0.038	0.0053
0.475	0.0287	0.0029	(0.019)	0.0052
0.633	0.02795	0.00365	(0.011)	0.0052
0.790	0.02725	0.00435	(0.008)	0.0052
0.790	0.0275	0.00435	(0.008)	0.0052
1.58	0.0241	0.0075	(0.002)	0.0052

acid + 0.040 molar sodium acetate, to which were added neutral salts

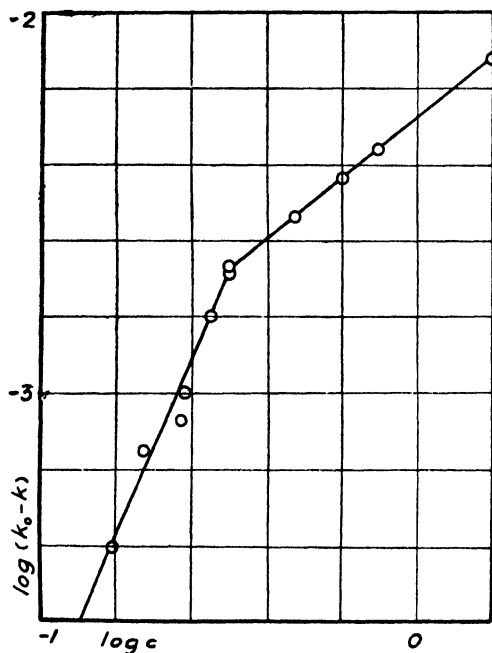


FIG. 2.

of various concentrations. The concentrations ( $c$ ) are expressed in mols per liter solution. The salts were Kahlbaum's "Zur Analyze" or preparations of similar purity.

*Sodium salts* ( $0 < c < 1$  normal) (Table III.) and *ammonium chloride* ( $0 < c < 1$  molar) had no effect, nor had addition of 0.25 molar *sucrose*.

*Lithium chloride* gave a decrease in the velocity. The difference between the constant for S.B. without LiCl  $k_0 = 0.0316$  and  $k$  for S.B. + LiCl is given in the third column of Table III. In Fig. 2,  $\log(k_0 - k)$  is plotted against  $\log c$ , where  $c$  is the concentration of LiCl. From  $c = 0.316$  to the highest concentration  $c = 1.58$ , the points fall

on a straight line. For  $c < 0.316$ , another straight line may be drawn

through the points. The accuracy of the values for  $k_0 - k$  at the smallest concentrations is small. The slopes of the two straight lines are 2.5 and 0.78, which give the following interpolation formulæ:—

$$\begin{aligned} c < 0.32 \text{ molar.} & \quad k_0 - k = 0.038 c^{2.5} \\ 0.32 \text{ m.} < c < 1.58 \text{ molar.} & \quad k_0 - k = 0.0052 c^{0.78} \end{aligned}$$

In the last two columns of Table IV.,  $(k_0 - k)/c^{2.5}$  and  $(k_0 - k)/c^{0.78}$  are given. There seems to be a sudden change from one formula to the other at 0.32 m. LiCl. It is surprising how well the formula  $k_0 - k = 0.0052 c^{0.78}$  holds even in very concentrated solutions.

*Potassium salts* give an increase in the velocity of the decomposition. For KCl,  $K_2SO_4$  and  $K_4Fe(CN)_6$ , the acceleration is proportional to the concentration of potassium ions when complete dissociation is assumed. Potassium ferricyanide seems to be an exception to the rule, for the acceleration is not proportional to the concentration. When  $\log(k_0 - k)$  is plotted against  $\log(3c)$ , the points fall on a straight line with the slope 0.8. The experimental data for the four salts are represented by the following interpolation formulæ:—

$$\begin{aligned} \text{S.B.} + \text{KCl} : & \quad k - k_0 = 0.0051 c \\ \text{S.B.} + \text{K}_2\text{SO}_4 : & \quad k - k_0 = 0.0050 (2c) \\ \text{S.B.} + \text{K}_3\text{Fe(CN)}_6 : & \quad k - k_0 = 0.0038 (3c)^{0.8} \\ \text{S.B.} + \text{K}_4\text{Fe(CN)}_6 : & \quad k - k_0 = 0.0044 (4c). \end{aligned}$$

*Caesium bromide* causes acceleration like potassium salts, but the effect is greater.

*Hexammin cobaltic chloride* accelerates about three times as much as potassium salts.

$BaCl_2$ ,  $MgCl_2$ ,  $MgSO_4$  and  $CaCl_2$  give retardation. For  $BaCl_2$  the effect is very small, only 4 per cent. in 0.5 molar  $BaCl_2$ . For the three other salts the experiments are represented by the following interpolation formulæ:—

$$\begin{aligned} \text{S.B.} + \text{MgCl}_2 : & \quad k_0 - k = 0.012c^{2/3}, & (0 < c < 0.5) \\ \text{S.B.} + \text{MgSO}_4 : & \quad k_0 - k = 0.016c & (0 < c < 0.2) \\ \text{S.B.} + \text{MgSO}_4 : & \quad k_0 - k = 0.0072c^{1/2}, & (0.2 < c < 0.5) \\ \text{S.B.} + \text{CaCl}_2 : & \quad k_0 - k = 0.0090c^{1/2}, & (0 < c < 0.5). \end{aligned}$$

*Copper salts* have a very great retarding influence on the decomposition of the nitroacetate ion, therefore the effect can be examined with much greater

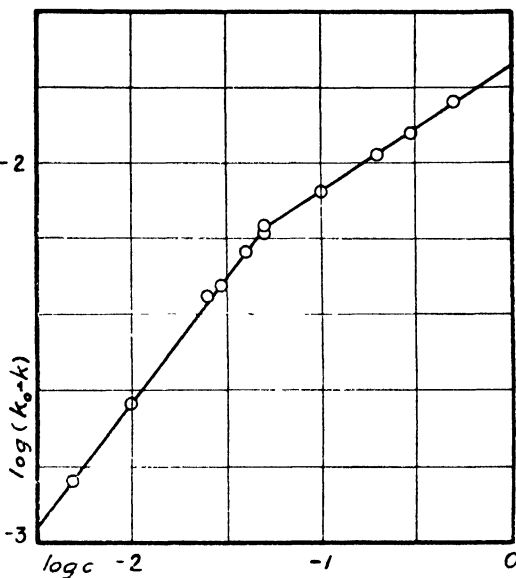


FIG. 3.

accuracy than usually. It seems as if the peculiarities found in the effect of salts of other bivalent metals are much more apparent with copper salts, and, therefore, copper salts were very useful for the study of this salt effect.

$\text{CuSO}_4$ .—The effect is very great (Table V.), and even in 0.1 molar  $\text{CuSO}_4$  it is 27 per cent. In Fig. 3,  $\log(k_0 - k)$  is plotted against  $\log c$ . The points fall on two straight lines having the slopes 0.33 and 0.67. Accordingly, the following formulæ hold:—

$$\begin{aligned} c < 0.048, & \quad k_0 - k = 0.0506c^{2/3} \\ 0.048 < c < 0.50, & \quad k_0 - k = 0.0182c^{1/3}. \end{aligned}$$

$\text{CuCl}_2$ .—The results of a series of experiments with S.B. +  $\text{CuCl}_2$  are represented by the three formulæ:—

$$\begin{aligned} c < 0.015, & \quad 0.03197 - k = 0.26 c. \\ 0.015 < c < 0.10, & \quad k_0 - k = 0.0318\sqrt{c}. \\ 0.05 < c < 0.5, & \quad k_0 - k = 0.0225\sqrt[3]{c}. \end{aligned}$$

TABLE V.

SOLUTION: S.B. +  $\text{CuSO}_4$ .

$c$ .	$k$ .	$k_0 - k$ .	$(k_0 - k)/c^{2/3}$ .	$(k_0 - k)/c^{1/3}$ .
0.0026	0.0308	0.0008	(0.04)	(0.006)
0.0050	0.03015	0.00145	0.050	(0.0085)
0.0102	0.0293	0.0023	0.049	(0.0106)
0.0251	0.02715	0.00445	0.051	(0.0152)
0.0300	0.0269	0.0047	0.049	(0.0158)
0.0400	0.02575	0.00585	0.050	(0.0171)
0.0500	0.02505	0.00655	0.048	0.0178
0.0500	0.0247	0.0069	0.051	0.0187
0.100	0.02315	0.00845	(0.039)	0.0182
0.200	0.02105	0.01055	(0.033)	0.0181
0.300	0.0195	0.0121	(0.027)	0.0181
0.500	0.0169	0.0147	(0.023)	0.0185

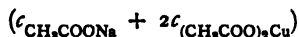
In Fig. 4,  $\log(k_0 - k)$  is plotted against  $\log c$ . The difference between  $\text{CuSO}_4$  and  $\text{CuCl}_2$  is very striking. In very dilute solutions of  $\text{CuCl}_2$ ,  $k_0 - k$  is proportional to the concentration of  $\text{CuCl}_2$ . For this linear part, the value  $k_0 = 0.03197$  has been used instead of the usual value  $k_0 = 0.0316$ . An extrapolation of the  $k$  values to  $c = 0$  gives 0.03197. The points fall on three straight lines having the slopes 1.00, 0.50 and 0.33, except between 0.05 and 0.10 m., where the points often do not fall on the lines but between the lines having the slopes 0.50 and 0.33.

For the more concentrated solutions, we get proportionality to the cube root of the concentration for  $\text{CuCl}_2$  as well as for  $\text{CuSO}_4$ , but the proportionality factor for the chloride is  $5/4$  times as great as that for the sulphate.

When the concentration of acetic acid in the buffer solution is increased the effect of the copper chloride is considerably diminished. The change in the effect of the  $\text{CuCl}_2$  depends chiefly on the concentration of the free acetic acid, only to a small extent on the concentration of sodium acetate and the hydrogen ion concentration.

*Copper Acetate.*—The conditions which govern the reaction seem rather complicated in the solutions which have hitherto been used, acetate ions and chloride or sulphate ions being present simultaneously. Some experiments were therefore carried out with copper acetate alone. The results of four

series of experiments are summarised in Table VI. Within each series, the concentration of acetic acid and the total concentration of acetate



are kept constant. In each series, the retardation is proportional to the

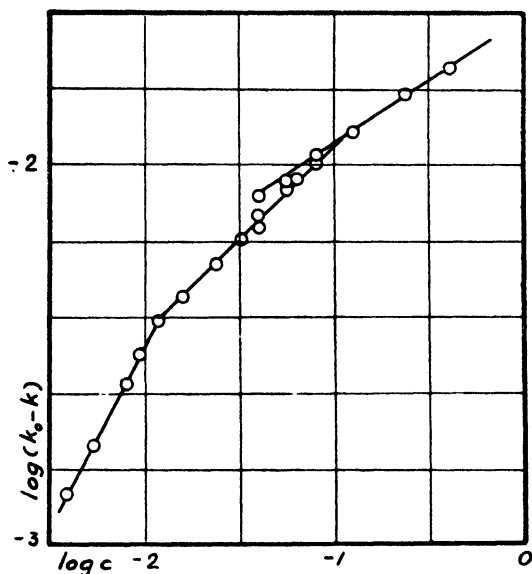


FIG. 4.

concentration of copper acetate, but the effect decreases with increase in the concentration of acetic acid, as shown in the table.

TABLE VI.

SOLUTION: COPPER ACETATE +  $\text{CH}_3\text{COONa}$  +  $\text{CH}_3\text{COOH}$ .

	I.	II.	III.	IV.
Concn. of acetic acid:	0.060	0.120	0.300	0.600
Total conc. of acetate:	0.040	0.100	0.250	0.400
$\{k_0 - k\}/c$ :	0.25	0.151	0.057	0.048

*Cobalt, Nickel, Lead, and Aluminium Salts.*—The retarding effect of  $\text{CoSO}_4$  is a little greater than that of Mg- and Ca-salts.  $\text{NiSO}_4$  has a greater effect than  $\text{CoSO}_4$ , and  $\text{Pb}(\text{NO}_3)_2$  a much greater effect.  $\text{AlCl}_3$  has a still greater effect, almost as great as  $\text{CuCl}_2$ . The reaction is not monomolecular, probably due to a slow hydrolysis of the  $\text{AlCl}_3$ . The hydrolysis is so great that it must affect the  $c_{\text{H}^+}$  of the buffer solution. Bjerrum<sup>11</sup> finds the constant of hydrolysis  $1.4 \times 10^{-5}$  at  $25^\circ$ .

### Discussion of the Effect of Salts on the Velocity of the Decomposition of the Nitroacetate Ion.

The above experimental results show that the salt effect is of an unusual type. Sodium salts (chloride, nitrate, and sulphate) have no effect

<sup>11</sup> *Z. physikal. Chem.*, 1907, 49, 336.

even in 1 *N*. solution. Potassium salts, caesium salts, and hexammin cobaltic chloride give an acceleration, in most cases proportional to the concentration. Ammonium chloride has no effect. Barium chloride and silver nitrate give a small retardation. Lithium, magnesium, calcium, cobalt, nickel, and lead salts give a considerable retardation. The effect seems mainly to depend on the cations. However, different salts of the same metal often give different effects as expressed by different powers of *c* in the formulas. This salt effect is of a distinctively individual character, the different salts of the same valence type giving quite different effects.

The kinetic salt effect usually found for reactions in aqueous solution is mainly due to the electric charges of the salt. In dilute solution it depends chiefly upon the valence type of the electrolyte, not upon the individual character of the ions. Thus sodium, lithium, and potassium ions give approximately the same effect in dilute solution. This ordinary salt effect, which depends on the activity coefficients of the substances involved, has especially been studied by Brønsted.<sup>12</sup> It can be divided into two groups:—

(1) The primary salt effect, which is the direct influence of an electrolyte on the velocity of the reaction of a molecule of the substance. The electrolyte causes a change in the chance of reaction without changing the concentration of the reacting substances.

(2) The secondary salt effect, which is the influence on the velocity by changing only the concentration of a reacting substance (ion or neutral molecule), not the chance of reaction of a given molecule. If the reacting substance is in equilibrium with other substances the addition of an electrolyte may displace the equilibrium, thus causing a change in the concentration of the reacting substances and accordingly in the velocity of the reaction.

In the experiments on the decomposition of nitroacetic acid in solutions of HCl we had a secondary kinetic effect. By addition of NaCl the equilibrium:  $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$ , where HX is nitroacetic acid, was displaced in favour of the ions. The velocity, which depends on the concentration of  $\text{X}^-$ , increased.

Brønsted,<sup>13</sup> has given a theory of the primary kinetic salt effect. For the reaction  $\text{A} + \text{B} = \text{C}$ , he obtains the expression:

$$v = k_{\text{ACB}} \frac{f_{\text{A}} f_{\text{B}}}{f_{\text{AB}}},$$

where  $f_{\text{A}}$ ,  $f_{\text{B}}$ , and  $f_{\text{AB}}$  are the activity coefficients of A, B and a critical complex of A and B. For a monomolecular reaction, we have:  $v = k_{\text{A}} f_{\text{A}} / f_{\text{X}}$ , where  $f_{\text{X}}$  is the activity coefficient of the critical complex. In the case of the decomposition of the nitroacetate ion we have approximately  $f_{\text{A}} = f_{\text{X}}$ , because A and X have the same charge. We thus obtain the equation  $v = k_{\text{A}}$ , that is, no salt effect. According to the activity rate hypothesis of Lewis and Harned<sup>14</sup> the velocity should be proportional to the activity of the reacting molecule or ion, that is,  $v = k_{\text{A}} f_{\text{A}}$ . It is clear from the experiments that there is no kinetic salt effect of this kind on the decomposition of the nitroacetate ion. The effect which has been found for a series of salts is decidedly not of this nature. It is much smaller and often of sign opposite to that which we should expect from the activity rate hypothesis. Thus by addition of 0.2 molar NaCl to the S.B. solution we

<sup>12</sup> *Z. physikal. Chem.*, 1924, **108**, 185.

<sup>13</sup> *Ibid.*, 1922, **102**, 169.

<sup>14</sup> *J. Chem. Soc.*, 1920, **117**, 1120; *J. Amer. Chem. Soc.*, 1922, **44**, 1475.

should expect a decrease in velocity of about 20 per cent., the activity coefficient of a monovalent ion like the nitroacetate ion being about 0.8 in 0.04 molar and about 0.65 in 0.24 molar mono-monovalent electrolyte. The fact that NaCl has no effect shows that a change in the activity coefficient of the nitroacetate ion does not affect the velocity of the decomposition.

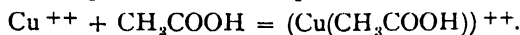
It has not been possible to find any explanation of the individual salt effect of the many salts examined in this work. The retardation caused by some of them is not merely due to the hydrolysis of the salts. This hydrolysis cannot increase the hydrogen ion concentration sufficiently for the production of so much undissociated nitroacetic acid that the decrease in velocity can be explained in this way. Carrara and Vespignani<sup>15</sup> find that copper sulphate in the concentration 0.2 m. at 25° is hydrolysed 0.057 per cent., which gives  $c_{H^+} = 0.00057 \times 0.2 = 10^{-4}$ . Even if the hydrogen ion concentration of the solution was increased to the value for  $c_{H^+}$  in the 0.2 m.  $CuSO_4$  in water only  $c_{H^+}/K = 10^{-4}/0.03 = 0.3$  per cent. of the nitroacetic acid would be undissociated, while the decrease in velocity is about 30 per cent.

The retardation might be due to a formation of complexes of the metal ion and the nitroacetate ion as for copper:  $Cu^{++} + X^- = (CuX)^+$ , where  $X^-$  is the nitroacetate ion. Only the free  $X^-$  reacts. This hypothesis is supported by the fact that copper ions, which have a very great kinetic effect, are very apt to form complexes, but silver ions, which also have a great tendency to form complexes, give a very small effect. A complex formation of this kind must be very sensitive to salt. According to the thermodynamic mass action law, we have:

$$\frac{c_{(CuX)^+}}{c_{Cu^{++}} \cdot c_{X^-}} = K_a \cdot \frac{f_1 \cdot f_2}{f_1} = K_a \cdot f_2,$$

where  $K_a$  is a true constant and  $f_1$ ,  $f_1'$  and  $f_2$  are the activity coefficients of  $X^-$ ,  $(CuX)^+$  and  $Cu^{++}$ . We have approximately  $f_1 = f_1'$ . Addition of salt will diminish the ratio  $c_{(CuX)^+}/c_{X^-}$ . More  $X^-$  is made active, the velocity increases. This was actually found by addition of NaCl,  $NaNO_3$  or  $Na_2SO_4$  to solutions of copper acetate. In agreement with the theory, NaCl and  $NaNO_3$  gave the same effect, while  $Na_2SO_4$ , which has a divalent ion, gave a greater increase.

Acetic acid diminishes the effect of copper ions. This might be explained by assuming formation of complexes such as:



A part of the copper ions are taken up by the acetic acid leaving less copper for the complex formation with nitroacetate ions. This equilibrium should not be salt sensitive in dilute solution because the electric charge is the same on either side.

As a test on this complex formation hypothesis, two experiments with hexammin cobaltic chloride,  $(Co(NH_3)_6)Cl_3$ , were carried out. In this salt Co has already taken up  $6NH_3$ , therefore it cannot take up any nitroacetate ions and should not cause any retardation. Actually it showed an acceleration.

No explanation is suggested for the acceleration which potassium salts, caesium bromide and  $(Co(NH_3)_6)Cl_3$  show. The order of the cations, Li, Na, K, Cs is that of the familiar lyotropic series, as found in so many connections.

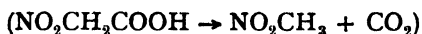
In the calculation of the dissociation constant of the nitroacetic acid from the velocity of the decomposition in solutions of HCl it has been assumed that hydrogen ions have no influence on the velocity of the decomposition of the nitroacetate ion. It is impossible to test this directly, but the results seem to justify the assumption.

It is most difficult to understand the reason for the discontinuities in the curves showing the effect of some salts. They are most striking for  $\text{CuSO}_4$  and  $\text{CuCl}_2$ . The breaks in the curves are so distinct and have been found in so many cases, for LiCl and for  $\text{MgSO}_4$  as well as for copper salts, that they almost seem to be real discontinuities. A more careful examination of the salt effect will soon be started by the writer in the Chemical Laboratory of the Royal Veterinary and Agricultural College in Copenhagen. In a later paper, it is hoped to discuss and explain the experimental results.

The examination of the salt effect described in this paper was intended to give a general idea of the different effects of many salts rather than a systematic and accurate examination of the laws which govern the salt effect. The experimental results have been expressed in simple formulæ, but it is not assumed that they are real laws.

### Summary.

The velocity of the decomposition of nitroacetic acid



in aqueous solution at  $20.00^\circ$  has been examined by measuring the pressure of carbon dioxide during the reaction.

The monovalent nitroacetate ion decomposes monomolecularly. The velocity constant  $k_0 = 0.0316$  ( $\text{min.}^{-1}$ , dekad. logs.) was found by experiments in certain buffer solutions in which all the nitroacetic acid was present as monovalent ion. The undissociated nitroacetic acid is stable in aqueous solution.

From experiments in strong acids the "concentration dissociation constant" of nitroacetic acid was calculated. The variations of this constant by addition of electrolytes were found to be in agreement with the theory of complete dissociation and interionic forces. In  $0.1\text{ }N$ . HCl the dissociation constant was found to be  $0.0340$ .

An examination of the effect of several salts on the velocity of the decomposition of the nitroacetate ion showed that some salts (e.g. sodium salts) have no effect, while others, as potassium salts, CsBr and  $(\text{Co}(\text{NH}_3)_6)\text{Cl}_3$ , give an acceleration. Most salts give a retardation, which is very great for copper salts. The effects were expressed in simple formulæ. This salt effect is of a new type, characteristic for each ion or salt.

In conclusion I wish to thank the Ramsay Memorial Fellowships Trust for a fellowship and the University of Bristol for hospitality during the time I spent there as Danish Ramsay Fellow. My thanks are especially due to Professor J. W. McBain for much help and interest in my work. I also wish to thank Professor J. N. Brønsted, Copenhagen, for parts of the apparatus for the measurement of the velocity of the reaction.<sup>16</sup>

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University of Bristol.*

<sup>16</sup> When this paper was ready for publication, two papers were published by *Y. Heuberger* (Svensk Kemisk Tidskrift, 1926, 38, 340-344 and 1926, 38, 378-384) on the decomposition of nitroacetic acid.

## REVIEWS OF BOOKS.

**Mechanics Applied to Engineering.** By JOHN GOODMAN. (London, 1926 : Longmans, Green & Co. Vol. I., ninth edition. Pp. ix + 853. 14s. 6d. net. Vol. II., pp. vii + 472. 16s. net.)

The eighth edition of this work was produced just before the war. In preparing the ninth edition the author was faced with the fact that his book already occupied nearly 900 pages, whilst there was new matter to be included and an insistent demand for worked-out examples of the mechanical principles treated. The problem was solved by placing the new matter in a separate volume. Volume II. contains also (and mainly) some 700 examples arranged under substantially the same chapter headings as serve for Vol. I. ; they are intended for the guidance of students who require something more than an elementary treatise but have little knowledge of higher mathematics.

Volume II. suffers from the defect that subjects which are not treated in Vol. I. are hidden amongst the 400 odd pages of numerical examples and since these examples are not too adequately indexed, are apt to be overlooked. Future editions would be improved if the 48 pages of unworked examples (and possibly the greater part of the appendix) in Vol. I. were removed to Vol. II. to make room for the new matter now included in Vol. II. As an example we find on p. 413 of Vol. II. the statement : "The question" of gradual stoppage in pipes . . . "is well worthy the attention of research workers"; but the exhortation is unlikely to reach the intended audience since it is lost in a mass of worked examples which, valuable though they be, will have little interest for the research worker.

The books are excellently produced at a very reasonable price.

**A Treatise on Light.** By R. A. HOUSTON. (London, 1927 : Longmans, Green & Co., Ltd. Fifth edition. Pp. 11 + 489. 12s. 6d. net.)

Small changes from the fourth edition have been made. The author has received many suggestions for alterations but has preferred not to deal exhaustively with subjects such as X-rays, relativity and quantum theory. The book is well produced. Of its usefulness no better criterion can be cited than the fact that it has passed through five editions in less than twelve years.

**National Physical Laboratory. Report for the year 1926.** (H.M.S.O., pp. 260. 7s. 6d. net.)

**The Kinetics of Chemical Change in Gaseous Systems.** By C. N. HINSHELWOOD, M.A. (Oxford, at the Clarendon Press, 1926. Pp. 204. Price 12s. 6d.).

The elucidation of the mechanism of chemical reaction is perhaps the most important and fundamental problem confronting the chemist. Even however in the cases most amenable to attack—reactions in gaseous systems—we are only in the preliminary stages of construction of a theory of reaction velocity, and baffling features present themselves in the simplest of chemical processes. The difficulties met with in formulating a mechanism of unimolecular reactions are

now well known. Difficulties of a different type appear in the interpretation of reactions between atoms, such as the formation of molecular bromine from bromine atoms. To take a third example, recent work evidencing the complex nature of solid catalytic surfaces appears unlikely to simplify the task of unravelling the mechanism of heterogeneous reactions.

These and their like are the problems dealt with in this book, which may unreservedly be recommended to those interested in this field and indeed to all students of physical chemistry. After an introduction in which are discussed those aspects of the Kinetic Theory needed for the subsequent development, follow chapters entitled: Bimolecular Reactions, The Energy of Activation, Termolecular Reactions, Unimolecular Reactions, the Kinetics of Heterogeneous Reactions and Activation in Heterogeneous Reactions. The subject matter is treated in a brief but clear manner, and the work forms an interesting and critical summary of our present knowledge of reactions in gaseous systems.

In the discussion of the mechanism of unimolecular processes it is concluded that "either some extended radiation theory is necessary, or reaction chains are possible." The only well established example of a unimolecular reaction at the time of publication was the decomposition of nitrogen pentoxide; since then, the author has discovered further examples in the decomposition of acetone and in the so-called "quasi-unimolecular" reactions, such as the decomposition of propionaldehyde. The latter are characterised by a unimolecular course at ordinary pressures, but at lower pressures they assume a bimolecular character. This later work has suggested the possibility that activation by collision may be faster than that previously thought possible. By assuming that the necessary energy of activation may be drawn from sufficient of the large number of degrees of freedom possessed by complex molecules, Hinshelwood and also Fowler and Rideal have demonstrated that activation may be maintained with sufficient rapidity to account for the experimentally determined velocity of reaction. Thus, in addition to the two alternatives cited above for the mechanism of unimolecular reactions, the third possibility of activation by collision remains in the field, and though this theory is not without difficulties of its own, it appears at present more likely to survive than the others.

For certain homogeneous bimolecular processes, of which the decomposition of HI, of  $N_2O$  and of  $Cl_2O$  are typical, the author shows that the ratio of effective to total collisions is equal to  $e^{-E/RT}$  where  $E$  is the energy of activation obtained from the Arrhenius equation  $\frac{d \log k}{dT} = \frac{E}{RT^2}$ . In such cases, the collision between reacting molecules may be the actual activating process, or molecules may be pre-activated either by radiation or by non-reactive collision. At present, we have no means of distinguishing between these possibilities. The author is perhaps over sanguine in one respect. It appears to the reviewer by no means so certain that even these comparatively simple bimolecular reactions are so independent of the presence of water vapour as might be inferred from the discussion (p. 103) on this point. In one case, the combination of hydrogen and iodine, a catalytic effect of moisture would appear to have been recently established.

R. O. G.

**Ancient Egyptian Metallurgy.** By Major H. GARLAND, O.B.E., M.C., F.C.S., AND C. O. BANNISTER, M.Eng., A.R.S.M., F.I.C. (London, 1927: C. Griffin & Co. Ltd.)

The late Major Garland, during the time he was stationed in Egypt as Superintendent of Laboratories at the "Citadel" had opportunities for examining ancient metal objects which few people are likely to meet. His work of preparing an account of his experiences in this direction was unfortunately stopped by his sudden death some six years ago. Fortunately however most of his notes were in such a condition that Prof. Bannister has been able to gather them together and to edit them to form this interesting book.

The most important of the author's conclusions is that iron must have been known and used in Egypt at a much earlier date than most archæologists suggest. Most metallurgists will agree with him in his contention that the remarkable sculptures in hard stone, such as diorite, which date from the fourth dynasty or the beautifully carved hieroglyphics in granite of the twelfth dynasty, photographs of which are reproduced, could only have been produced by the use of chisels made of iron and probably more or less carburised during manufacture. The possibility of producing such carvings by the use of copper saws fed with emery, as has been suggested by a well-known archæologist, seems rather fantastic, as the author says. Other interesting facts brought out are the very early use of the "cire perdue" process for castings and the comparatively late use of cold working associated with annealing for the shaping of vessels. All the early vessels appear to be castings. The author also shows the value of metallography in the examination of specimens of ancient metals, particularly with regard to deciding how they have been made; incidentally he also shows that the ideas of archæologists in this respect are not always correct.

J. H. G. M.

**Metallographic Researches.** By CARL BENEDICKS. (New York, 1926: McCraw Hill Book Co. Inc. \$4.00 net. 20s. net.)

During 1925, Professor Benedicks gave a series of lectures on metallurgical subjects to a number of educational and technical institutions and societies in the United States. The lectures were largely founded on original work which had been carried out at the Metallografiska Institutet, Stockholm; as much of this work had not been published in English, a number of requests were made that the lectures should be made accessible in printed form and as a result, we have the book recently published under the above title.

The contents cover a range of subjects of varied interest to the metallographer. Each of the eleven chapters, into which the book is divided, deals with some particular subject; they treat of such diverse things as the kinetic constitution of solid matter, homogeneous thermoelectric and electrothermal effects, hardness in metals and its cause, meteoric iron and invar, high power microscopy, thermal curves, specific gravity of molten iron and some consideration of the Ludwig-Soret phenomenon and its application to metallurgy.

Probably one of the most interesting chapters is that relating to the hardness of metals in general and of steels in particular. In this the author criticises some of the modern ideas with regard to hardened steel. Briefly his idea is that firstly the hardening effect of a solute on a solvent depends on its range of solubility; when the solubility of the added element B in A is small the hardening coefficient C is large. Secondly he regards austenite as a supercooled but not necessarily

supersaturated solution of carbon (or carbide) in  $\gamma$ -iron and martensite as a supersaturated but not supercooled solution in  $\alpha$ -iron. The range of solubility of carbon in  $\gamma$ -iron is great, hence the hardening coefficient of carbon on  $\gamma$ -iron is small; on the other hand carbon is only slightly soluble in  $\alpha$ -iron hence the supersaturated solution in  $\alpha$ -iron, existing in martensite of fairly high carbon content, is very hard. He applies similar reasoning to explain the hardness increase in duralumin and in alloys of aluminium with zinc and copper respectively. The author sets out his views quite clearly, though some of his statements appear to rest on rather slender foundation; for example, the displacement of the *alpha* range into higher temperatures by the addition of tungsten is adduced as "the physico-chemical reason for the existence of red hardness in high-speed tool steel." Here, however, the author would appear to have doubts himself about his statement for, by way of after-thought, he mentions the high melting-point of tungsten as being related to the same thing; this further explanation, however, overlooks the fact that chromium, whose melting-point does not differ greatly from that of iron, induces a very notable amount of red hardness in steel when added to the latter.

Metallurgists in general will read Professor Benedicks' book with great interest, not of course because it is in any sense a text-book of metallography, but because it contains an account of the experimental work and the ideas of a man of singularly broad vision on a number of varied but interesting metallographical topics.

J. H. G. M.

**The Metallurgy of the Common Metals.** By LEONARD S. AUSTIN. Sixth Edition. (New York, 1926: John Wiley & Sons, Inc. London: Chapman & Hall, Ltd.)

This edition follows the same general lines as the preceding editions, but the text has been revised to bring it into accord with present-day practice. The book is primarily addressed to students of mining and is intended to give them a general outline of the metallurgy of the common metals gold, silver, iron, copper, lead, and zinc. It appears to fulfil its purpose quite well though the chapters dealing with the metals with which the author has had greater personal experience, *e.g.* copper, are better than those for which he has had to depend to a considerable extent on second-hand information. It might also be borne in mind that the book describes, almost entirely, American metallurgical practice.

J. H. G. M.

# THE THEORY OF STRONG ELECTROLYTES.

## A GENERAL DISCUSSION.

A GENERAL DISCUSSION on the "THEORY OF STRONG ELECTROLYTES" was held by the Faraday Society on Friday, 22nd April and Saturday, 23rd April, 1927, in the Department of Biochemistry University Museum, Oxford. The President of the Society, **Professor C. H. Desch, D.Sc., F.R.S.**, was in the Chair.

The subject was considered under two main headings:—

### Part 1. **Mobilities of Ions.**

Introduced by Dr. E. Hückel (a communication from Professor P. Debye).

(Friday, 22nd April, 3.30-7.15 p.m. and Saturday, 23rd April, 9.30-11 a.m.)

### Part 2. **Activity.**

Introduced by Professor J. N. Brønsted.

(Saturday, 23rd April, 11.15 a.m.-1 p.m. and 2 p.m.-3.45 p.m.)

**The President** in opening the proceedings extended a hearty welcome on behalf of the Society to the many distinguished visitors who had been able to accept the invitation of the Society to be present. He especially welcomed Professors Bjerrum, Brønsted, Fajans, Harned, Hevesy, Remy, and Scatchard, and Doctors Christiansen, Hückel, Onsager, and Ulich.

The papers contributed to the Meeting and a full report of the Discussion will be found in the succeeding pages.

The President in bringing the proceedings to a close asked the Society to accord its thanks to those who had contributed papers and particularly to those who had come from abroad to contribute to the discussion. The proposal was received with acclamation. A similar reception was accorded to the proposal that the thanks of all present be accorded to the Rector and Fellows of Lincoln College, the Principal and Fellows of Jesus College, and the Rector and Fellows of Exeter College, as well as to Sir Charles Sherrington and Professor C. A. Peters, for the hospitality so generously afforded to the Society and its guests.

**Professor Brønsted** on behalf of the foreign guests expressed their gratitude for and appreciation of the privilege of being present. He felt sure also that all the foreign guests wished also to join with the President in thanking their colleagues at Oxford for the very kind hospitality which had been extended to all of them.

**Professor Bjerrum** briefly associated himself with Professor Brønsted's remarks, and wished success to the Faraday Society.

INTRODUCTORY PAPER—PART I: MOBILITIES OF IONS.  
REPORT ON CONDUCTIVITY OF STRONG ELECTROLYTES IN DILUTE SOLUTIONS.

By P. DEBYE.

(Received March 28th, 1927.)

1. It is a well-established fact, that the change of the *activity coefficient* of ions with concentration in highly dissociated solutions can be represented by a square root law. The experimental evidence supports the view that for the change in *conductivity* of strong electrolytes with concentration Kohlrausch's square root law holds. The interionic attraction theory of activity gives an explanation of the square root law, based on the fact that the thickness of the ionic atmosphere of mean charge surrounding each ion has to be proportional to the square root of the concentration, if the principal forces between ions are the ordinary Coulomb forces. In this way, remembering that Coulomb's law puts the forces inversely proportional to the square of the distance, a close correspondence is brought forward between the exponent 2 in this law and the exponent  $\frac{1}{2}$  of the concentration in the activity law. The occurrence of the same exponent in Kohlrausch's law makes it at once probable that its explanation has to be found along the same lines. This report contains an account of the reasoning by which Coulomb's law and the square root law in conductivity have been connected.

2. In the following pages it will be necessary to refer constantly to what we will call the ionic atmosphere and the space distribution of its charge density. We may therefore begin by defining this density. Suppose a straight line of length  $r$  connected with the ion in such a way, that during the migration of the particle the direction in space of this line as well as its length is always kept the same. At the end of this line we imagine an element of volume. Now considering the ion with its element for a certain time, we find that sometimes an excess of positive and sometimes an excess of negative electric charges is contained within the element. Taking the time integral of this charge and dividing this integral by the whole time of observation, we obtain the mean charge of the element of volume. What we call the density of the ionic atmosphere is this mean charge divided by the volume of our element. It is obvious that so far as Coulomb forces alone are considered the density in the ionic atmosphere will be of opposite sign to the charge of the central ion and will increase with decreasing distance from the centre.

3. Between the electrostatic potential at the surface of the ion in an infinitely dilute solution (considering the ion for the sake of clearness of the underlying picture as a sphere with a surface charge) and this potential for a finite concentration will exist a difference due to the existence of the oppositely charged ionic atmosphere. The whole charge of this atmosphere must necessarily be equal and opposite to the charge of the central ion.

So the difference between the two potentials, *i.e.*, the potential due to the atmosphere, will depend chiefly on the distance over which this total charge is spread out. Under certain limiting conditions, which we have not to discuss here, it is possible to show that the significant factor in representing the decrease in density with the distance is the exponential  $e^{-\kappa r}$ , wherein  $\kappa$  has the dimension of a reciprocal length and is given by the formula,

$$\kappa^2 = \frac{4\pi}{DkT} \sum n_i e_i^2$$

( $D$  = dielectric constant of the solvent,  $k = 1.37 \times 10^{-16}$  = Boltzmann's constant,  $T$  = absolute temperature,  $n_i$  = number of ions of kind  $i$  in 1 c.c.,  $e_i$  = charge of one ion of kind  $i$ .)

For a uni-univalent electrolyte of concentration  $\gamma$  calculated in mols. per litre and in the solvent water, we find

$$\kappa = 3.27 \cdot 10^7 \sqrt{\gamma} \frac{1}{\kappa} = \frac{3.06 \cdot 10^{-8}}{\sqrt{\gamma}} \text{ cm.}$$

We will call the length  $\frac{1}{\kappa}$  the radius of the ionic atmosphere.

As the potential due to a charge  $E$  at a distance  $r$  in a medium of dielectric constant  $D$  is equal to  $\frac{E}{Dr}$ , we should expect that the potential of the central ion due to the charged atmosphere of thickness  $\frac{1}{\kappa}$  is proportional to

$$-\frac{E\kappa}{D}.$$

It can be shown that this potential is not only *proportional* to the given expression, but that it is *exactly equal* to it, if now by  $E$  we denote the charge of the central ion. The activity of an ion is very closely connected with its potential and as  $\kappa$  is proportional to the square root of the concentration, the given expression involves an explanation for the square root law in activity.

4. Now coming to the discussion of the interionic attraction theory of conductivity, we may begin with the statement that in a most general way the conductivity  $\lambda$  of any electrolyte solution can always be expressed by the formula

$$\lambda = \sum \frac{n_i e_i^2}{\rho_i}$$

( $\lambda$  = conductivity,  $n_i$  = number of ions in 1 c.c. of kind  $i$ ,  $e_i$  = charge of one ion of kind  $i$ ,  $\rho_i$  = friction coefficient of an ion of kind  $i$ . The notation  $\rho_i$  is introduced in such a way that  $\rho_i$  multiplied by the mean velocity of the ion in the direction of the external force gives the frictional force in the medium, which has to be overcome during the steady motion.)

Obviously we have two possibilities, in trying to explain how the conductivity will change with the concentration. We can first consider the number of ions  $n_i$  as variable, which is the way of the classical theory supposing a thermodynamic equilibrium between the undissociated molecule and the dissociated ions. But secondly it is also possible to focus attention on possible changes with concentration of the friction coefficients  $\rho_i$  or their reciprocals, the mobilities. Now the theory of the square root law

in activity has to be built up on the assumption of total dissociation, and we must therefore make the same assumption in the case of strong electrolytes. But this assumption involves that  $n_i$  is exactly proportional to the total concentration. To explain the deviations of the proportionality between the conductivity and the concentration, therefore, only the second possibility is left.

5. Let us consider the ionic atmosphere again. In the equilibrium case this atmosphere has central symmetry. Applying an external field, so as to create a current and a mean movement of each ion in one direction, we may expect that the central symmetry will be destroyed. In fact, if for instance the central ion moves to the right, then during its motion it will constantly have to build up a charge density constituting its atmosphere to the right, whereas to the left the charge density will have to die out. Of course if the creation of the ionic atmosphere could be done instantaneously no effect of the motion would be perceptible. But if a finite time of relaxation, as we will call it, exists, during the motion of the central ion the atmosphere will in the right-hand part never reach its equilibrium density, whereas in the left-hand part the density will constantly be larger than its equilibrium value. If now we remember the fact that the charge density in the atmosphere always has a sign opposite to the charge of the ion, we see at once that, owing to the dissymmetry of its atmosphere, the central ion will be acted upon by a force tending to *decrease* its velocity. As the amount of dissymmetry increases with increasing velocity, this force will also increase, so that it will have the same effect as an increase of the friction constant would have.

This reasoning having shown that a change of mobility with concentration may indeed be expected, provided a time of relaxation characteristic of the ionic atmosphere exists, we will now consider the process of an ion building its atmosphere.

6. The question we have to consider is essentially that of finding an expression for the space distribution of ions not in the equilibrium case but taking into account its variation in time. Therefore we cannot appeal to the Maxwell-Boltzmann function. However in the general equations describing the Brownian movement we possess a more general mathematical tool, which can lead us to an answer. In this way the details of the following statement can be worked out.

Suppose a charge  $E$  (of small dimensions) has been long enough at some point of the liquid, so that its ionic atmosphere has reached its equilibrium value. Now let us annihilate this central charge at the instant  $t = 0$ . We will ask how the charge density of the atmosphere spreads out to zero density. The mathematical expression for the charge density or the potential as a function of the distance from the centre  $r$  and the time  $t$  turns out not to be very simple. The principal point however is, that there exists an essential time constant  $\tau$  governing the decrease. We will call this constant the time of relaxation; in the case of an electrolyte with two univalent ions of equal mobility (like KCl)  $\tau$  is given by the expression,

$$\tau = \frac{\rho}{\kappa^2 k T}.$$

For a KCl solution of concentration  $\gamma$  mols. per litre, this gives

$$\tau = \frac{0.55}{\gamma} \cdot 10^{-10} \text{ sec.}$$

The following table shows the values of the potential  $\psi$  at a distance  $r = \frac{1}{\kappa}$  (the radius of the ionic atmosphere) divided by the potential  $\psi_0$  at the instant  $t = 0$  for different times  $t$  and for a millimolar KCl solution.

$t$	0	0.068	0.136	0.204	0.272	0.408	$\left\{ \begin{array}{l} 0.544 \\ 10^{-7} \text{sec.} \end{array} \right.$
$\frac{\psi}{\psi_0}$	1	1.14	1.02	0.826	0.666	0.445	0.307

Even for this millimolar solution the time of relaxation is only of the order of magnitude  $10^{-7}$  seconds. If in such a solution we apply an external field of 1 volt/cm. an ion will obtain a velocity of  $6.7 \cdot 10^{-4}$  cm/sec., so that it will take  $1.4 \cdot 10^{-3}$  seconds to travel over a distance equal to the radius of the ionic atmosphere. At first glance, it is obvious that there will be only a very slight dissymmetry in the charge density distribution of the ionic atmosphere and it seems improbable that the apparent change in mobility due to this dissymmetry should be appreciable. However this attitude changes if we evaluate the magnitude of the force in the vicinity of an ion. If the dissymmetry were large enough to be compared with a concentration of the charge of one single ion ( $4.77 \cdot 10^{10}$ ) at a distance equal to the radius of the ionic atmosphere from the central ion ( $97 \cdot 10^{-8}$  cm.), this particle would be in a field of 1900 volts/cm. So we understand how even a slight dissymmetry will be sufficient to create an appreciable additional force owing to the relatively enormous value of the elementary electronic charge.

7. The same general equations, which gave us the information for the foregoing discussion, enable us also to calculate the stationary dissymmetry around an ion, which we move with a given constant velocity  $v$  in the direction of the external field. We find a dissymmetry of the kind expected, which in a diagram of lines of force could be described as a slight bending of these lines away from the direction in which the ion proceeds. The additional field intensity is in the direction opposite to the mean velocity of the central ion and is given by the expression,

$$F_1 = - \frac{1}{6} \frac{E}{D} \frac{\kappa \rho}{kT} v,$$

if  $E$  is the charge of the central ion and  $\rho$  is a mean friction coefficient of the solution, calculated according to the formula,

$$\rho = \frac{\sum n_i e_i^2 \rho_i}{\sum n_i e_i^2}.$$

For a KCl solution in which the ions have equal mobilities we can easily compare the additional force, *i.e.*, the product of the ionic charge and the additional field intensity, with the friction at force  $R_0 = \rho v$  in infinitely dilute solution. This quotient is given by the expression,

$$\frac{EF_1}{R_0} = - \frac{E' \kappa}{6DkT},$$

which has the absolute value  $0.384 \sqrt{\gamma}$  for a KCl solution in water of concentration  $\gamma$  mols. per litre, showing that the effect is of practical importance.

In our note on the subject we took the sum of the external field intensity  $F_0$  and this calculated additional field intensity  $F_1$  as the total field intensity acting on the central ion. Here it is that a criticism of Onsager enters. His argument is that an ion which is moved with constant velocity in a solution is not strictly the same as a real ion, which besides its mean motion in one direction also possesses a Brownian movement. This irregular motion can indeed be expected to have an effect on the dissymmetry of the ionic atmosphere. Onsager calculates, for instance, that for a uni-univalent electrolyte our expression has to be multiplied by the numerical factor  $2 - \sqrt{2} = 0.586$ . For details I refer to Onsager's own report

8. Thus far we have focussed our attention on the electric forces acting on an ion. But in the steady state of motion these forces have to be in equilibrium with the force due to the impacts of the surrounding molecules introduced as a frictional force. In an infinitely dilute solution we can formally put this frictional force on a central ion, say of charge  $E$  and friction constant  $P$ , equal to

$$R_0 = Pv,$$

because this is the only expression which will lead to Ohm's law. But it is consistent with Ohm's law that in a solution of finite concentration the apparent frictional constant may be different from its limiting value  $P$ . To find the amount of this supposed difference it seems necessary to start with a definite picture and so we treated the case of a charged sphere of radius  $C$  moving with a constant velocity under the influence of a constant external electrical field of intensity  $F_0$  in a solvent containing ions. Now around this particle there will again exist an ionic atmosphere, supplying the elements of volume of the liquid with a charge density. In Stokes' formula, giving for the frictional force the expression,

$$R_0 = 6\pi\eta Cv$$

( $\eta$  = internal friction constant of the liquid),

it is supposed that on the elements of volume of the liquid no external force acts at all. But in our case such forces exist, since the external electric field will act on the charges constituting the atmosphere. That is why a new calculation had to be carried out. This calculation is however a familiar one, as it is essentially similar to the calculation carried out by Helmholtz in his theory of electrophoresis. It is even sound to say that no essential difference exists between the well-known Helmholtz double layer and our ionic atmosphere and that the principal part of the interionic attraction theory really is a theory of that part of a Helmholtz double layer which extends in the solution surrounding each ion.

The charges in the liquid and the charge of the sphere always have opposite sign. The additional motion due to the existence of these charges will therefore have velocities oppositely directed to the velocity of the particle and we have to expect an increase in the apparent frictional force. That results also from the calculation, from which it follows that, in addition to the Stokes' force  $R_0 = 6\pi\eta Cv$  an additional force,

$$R_1 = EF_0C\kappa,$$

will act in a direction opposite to the direction of motion. We found for a uni-univalent solution in water,

$$\kappa = 3.27 \cdot 10^7 \sqrt{\gamma}.$$

The additional force will in this case be represented by the expression,

$$R_1 = EF_0 \cdot 0.327 \cdot 10^8 C \sqrt{\gamma},$$

showing that for particles of the size of ions (i.e., values of  $C$  of the order  $10^{-8}$  cm.) this additional force will also be of practical importance.

9. The only thing left now is to combine all results and to calculate the migration velocity of the central ion from the condition that the whole electric force  $E(F_0 + F_1)$  has to be equal to the whole frictional force  $R_0 + R_1$ , giving the equation,

$$EF_0 - \frac{E^2}{6D} \frac{\rho\kappa}{kT} v = Pv + EC\kappa F_0,$$

if we use the value of  $F_1$  given in our first paper. Hence it follows that the migration velocity of an ion with charge  $E$  and the frictional constant  $P$  should be represented by the formula,

$$v = \frac{EF_0}{P} \frac{1 - C\kappa}{1 + \frac{\rho}{P} \frac{E^2\kappa}{6DkT}} = \frac{EF_0}{P} \left[ 1 - C\kappa - \frac{\rho}{P} \frac{E^2\kappa}{6DkT} \right].$$

The principal feature of this formula is the fact that the correction of the migration velocity in infinite dilution is proportional to  $\kappa$  (the reciprocal of the radius of the ionic layer) and therefore proportional to the square root of the concentration. So it seems proved that the interionic attraction theory is adequate to explain Kohlrausch's law.

This granted, our attention will be drawn to the numerical value of the factor entering in this law. To bring out more clearly the different remarks made about the theory of that factor in the literature since our first note appeared, we will confine ourselves to the case of a uni-univalent electrolyte. Calling  $\Lambda_0$  the limiting value of the molar conductivity at infinite dilution and  $\Lambda$  the molar conductivity at a certain (small) concentration, the original theory leads, according to the given expression for the migration velocity, to the formula,

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[ \frac{C_1\rho_2 + C_2\rho_1}{\rho_1 + \rho_2} + \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \frac{e^2}{6DkT} \right] \kappa,$$

or, substituting numerical values for solutions in water at  $18^\circ \text{C}$ .,

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[ 0.233 \cdot 10^8 \frac{C_1\rho_2 + C_2\rho_1}{\rho_2 + \rho_1} + 0.273 \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \right] \sqrt{2\gamma}.$$

What we tried to show was the fact that the experimental values found for the factor  $\sqrt{2\gamma}$  are such that they are not in contradiction with values of the radii  $C_1$  and  $C_2$  of the order of magnitude  $10^{-8}$  cm. Thus for instance, in KCl solutions the experimental factor is equal to 0.461 and because  $\rho_1 = \rho_2$  the theoretical factor equals

$$0.233 \cdot 10^8 \frac{C_1 + C_2}{2} + 0.273,$$

hence  $\frac{C_1 + C_2}{2}$  had to be taken equal to  $0.79 \times 10^{-8}$  cm. We preferred this attitude, because we did not feel confident that the calculation of the additional frictional force with the help of the ordinary hydrodynamical equations could give us correct values in the domain of molecular dimensions. If however this objection is not taken seriously, it is possible

### 340 CONDUCTIVITY OF ELECTROLYTES IN SOLUTIONS

to avoid the introduction of the ionic radii  $C_1$  and  $C_2$ , because then according to Stokes' formula,

$$\rho_1 = 6\pi\eta C_1, \quad \rho_2 = 6\pi\eta C_2,$$

and the radii will be eliminated provided the internal frictional constant  $\eta$  is taken as the ordinary value of our macroscopic experiments. Performing this elimination gives the formula,

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[ \frac{1}{3\pi\eta} \frac{Ne^2}{\Lambda_0} + \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \frac{e^2}{6DkT} \right] \kappa,$$

in which  $N = 6.06 \times 10^{23}$  = Avogadro's number, or substituting numerical values and expressing  $\Lambda_0$  in practical units,

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[ \frac{35.6}{\Lambda_0} + 0.273 \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \right] \sqrt{\frac{1}{2\gamma}}.$$

However in this way the factor comes out somewhat too large, giving for instance for KCl solutions 0.547 instead of the experimental value 0.461. On the other hand the experimental values support the view that a connection may exist between the factor in Kohlrausch's law and the absolute size of the limiting value for the molar conductivity of the kind indicated in the foregoing formula. This led Redlich to the assumption that for molecular dimensions Stokes' law should be written in the form,

$$\rho = \frac{1}{\phi} 6\pi\eta C,$$

with a numerical factor  $\phi$ . He claims that for uni-univalent electrolytes and with  $\phi = 0.694$ , it is possible to calculate the values of the factor in Kohlrausch's law, which takes the form,

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[ \frac{0.694}{3\pi\eta} \frac{Ne^2}{\Lambda_0} + \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \frac{e^2}{6DkT} \right] \kappa,$$

or substituting numerical values and expressing  $\Lambda_0$  in ordinary practical units,

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[ \frac{24.7}{\Lambda_0} + 0.273 \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \right] \sqrt{\frac{1}{2\gamma}}.$$

The most recent suggestion is made by Onsager. As was already pointed out, he shows that taking into account the Brownian movement of the central ion the value of the additional force due to the dissymmetry of the ionic atmosphere has to be corrected. If the mobilities of the two ions are equal his correction factor has the value  $2 - \sqrt{2} = 0.586$ . Now introducing this correction, but making no correction at all regarding Stokes' law, the theoretical expression in the case of KCl ( $\rho_1 = \rho_2$ ) becomes

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[ \frac{35.6}{\Lambda_0} + 0.160 \right] \sqrt{\frac{1}{2\gamma}},$$

which gives for  $\Lambda_0 = 129.9$  the value 0.433 for the factor which is close to its experimental value 0.461. For further interesting details of this recent promising development I can refer to Onsager's own report.

*Madison (Wis.).*

# REPORT ON A REVISION OF THE CONDUCTIVITY THEORY.

By L. Onsager.

(Received 21st March, 1927.)

**Introduction.**—This paper presents a modification of the Debye-Hückel theory for the conductivity of strong electrolytes.

Debye and Hückel start from the assumption, that the fall in molar conductivity which occurs with increasing concentration is chiefly due to the electrostatic forces between the ions.

As Debye has told you in his paper, the velocity of an ion in a conducting electrolyte will be affected by its ionic atmosphere in two different ways. Firstly, as the ion moves, the concentration disturbance in its neighbourhood must be forced to move with the same velocity; so the moving ion will be exposed to electric forces from the surrounding ones. Secondly, the surrounding ions, by the action of an external electric field, will cause an additional movement of the solvent, this second effect corresponding to the phenomenon generally known as electrophoresis. For both effects, the resultant decrease in molar conductivity is proportional to the square root of concentration. This gives a limiting formula for the molar conductivity:

$$\bar{\Lambda} = \bar{\Lambda}_0 - a\sqrt{\Gamma} \quad (1)$$

where  $\bar{\Lambda}$  = the molar conductivity,  $\Gamma$  = twice the ionic strength. This formula was found, many years ago, empirically and thoroughly tested by Kohlrausch. However, according to Debye and Huckel, it is not possible to determine the value of the factor  $\alpha$  otherwise than from the conductivity measurements themselves, because the formula for the electrophoretic effect involves the radius of the ion. Now, we may try to compute that radius from the mobility of the ion, but the value of  $\alpha$  which we find in that way, does not agree with the experiments, the calculated decrease in conductivity being always too great, though the order of magnitude comes out right.

1. *Electrophoresis*.—A year ago I published a paper,<sup>1</sup> showing that it is possible to compute the electrophoretic effect in such a way that the result in the limiting case of small concentrations will be independent of the ionic radius. We shall only consider the result of that deduction; in the limit of small concentrations, the additional velocity given to the ion by electrophoresis is found equal to:

$$\Delta v_j = - \frac{X_{e,\kappa}}{6\pi\eta} \quad (2)$$

where  $X$  = strength of the electric field,  $e_i$  = the charge of the ion in question,  $\eta$  = the viscosity, and  $\kappa$  = the mean inverse radius of the ionic atmosphere. Formula (2) is essentially the same as that previously found by Debye and Hückel. They found for the force caused by electrophoresis:

$$-e X_{\kappa b} \cdot \cdot \cdot \cdot \cdot \cdot (3)$$

<sup>1</sup> *Physik. Z.*, 1926, **27**, 388.

where  $b$  = ionic radius. Indeed if we take :

$$\rho = 6\pi\eta b,$$

according to Stokes' formula, for the friction coefficient of the ion, then we get :

$$\rho \Delta v_j = 6\pi\eta b \Delta v_j = - e_j X_{\kappa} b \quad . \quad . \quad . \quad (4)$$

for the corresponding force. Of course, if the Stokes' law does not hold, formula (3) is wrong too, but the validity of formula (2) is not affected.

So we have to look elsewhere for an explanation of the reason why the value of  $\alpha$  in formula (1), as calculated by Debye and Hückel, does not fit in with the experimental facts.

2. *Ionic Forces*.<sup>1</sup>—We are going to show that the method used by Debye and Hückel to compute the first effect mentioned in our introduction needs some modification for fundamental reasons.

To begin with, we shall consider a simple condition which the electrical forces between the ions have to fulfil, that is the condition of equilibrium. It is evident, that the internal forces between the ions form an equilibrium group—as it also follows from Coulomb's law—so, the resultant of all the forces exerted by the cations upon the anions must be equal to that exerted by the anions upon the cations.

Now Debye and Hückel try to compute the forces arising between the ions in a conducting electrolyte, by considering an ion moving with constant velocity along a straight line through the electrolyte, and calculating the force acting upon it from the surrounding ions. For an ion with the charge  $e_j$  moving with the velocity  $v_j$  this force will be (provided the concentration is small enough) :

$$- \frac{e_j^2 \kappa}{6DkT} \rho_m v_j$$

where  $D$  = the dielectric constant,  $T$  = the absolute temperature, and  $k$  = Boltzmann's constant ;  $\rho_m$  is a mean frictional coefficient of the ions in the electrolyte. However, formula (4) fits in with the equilibrium condition mentioned above only in special cases ; for instance, in the case of a simple binary electrolyte with one kind of anions and one kind of cations, the equilibrium condition is only fulfilled when the velocities of anions and cations are equal (in opposite directions).

A closer analysis of the problem<sup>2</sup> leads to the conclusion that, to calculate the resistance upon an anion moving through an electrolyte, we must take into account its own Brownian movements. If we suppose the ion constrained to follow a given path, thus suppressing its Brownian movements, we shall always get too high a value for the resistance. A further correction must be introduced for the migration of the ions forming the atmosphere.

The diffusion of two ions in relation to one another will cause a combined relaxation of both ionic atmospheres. So, instead of the separate differential equations found by Debye and Hückel for the fields of each ionic atmosphere, we get a system of simultaneous linear differential equations for all atmospheres together. In the most simple case, when only two kinds of ions are present, the separation is carried out very easily, and gives the following expression for the strength of the additional electric field caused by the atmosphere :

<sup>2</sup> For an extensive treatment of the problem see : Onsager, *Physik. Z.*, 1927, 28, 277-

$$\Delta X = \frac{4\pi}{D^2 k^2 T^2} \frac{\frac{\rho_2}{\rho_1} - \frac{e_1}{e_2}}{\frac{1}{\rho_1} + \frac{1}{\rho_2}} \frac{(n_2 e_2) e_1 e_2}{3(\kappa + \kappa')} X = \frac{e_1 e_2}{3 D k T} \frac{\kappa'^2}{\kappa + \kappa'} X. \quad (5)$$

where  $\rho_1, e_1$  and  $n_1$  signify frictional coefficient, charge and concentration of the anions, and  $\rho_2, e_2$  and  $n_2$  are the corresponding characteristics of the cations. According to Debye and Hückel we put:

$$\kappa^2 = \frac{4\pi}{D k T} (n_1 e_1^2 + n_2 e_2^2);$$

the quantity  $\kappa'$  differs from  $\kappa$  by a numerical factor; it is given by the equation:

$$\kappa'^2 = \frac{4\pi}{D k T} \frac{\frac{n_1 e_1^2}{\rho_1} + \frac{n_2 e_2^2}{\rho_2}}{\frac{1}{\rho_1} + \frac{1}{\rho_2}}.$$

In accordance with the equilibrium condition  $\Delta X$  is equal for both kinds of ions. In the case of binary electrolytes, equation (5) becomes simplified as follows:

$$\Delta X = - \frac{e^2}{6 D k T} (2 - \sqrt{2}) \kappa X \quad (6)$$

In this case  $\kappa'^2$  always equals  $\frac{\kappa^2}{2}$ . This result may be compared with that found by Debye and Hückel:

$$\Delta X_1 = - \frac{e^2 \kappa}{6 D k T} \frac{\rho_m X}{\rho_1} \quad (7)$$

for binary electrolytes in which case  $\rho_m = \frac{\rho_1 + \rho_2}{2}$ . The difference between expressions (6) and (7) is that the former contains the factor  $2 - \sqrt{2}$  instead of the factor  $\frac{\rho_m}{\rho_1}$  in (7).

3. *Mobility Formulæ.*—In writing formulæ for practical use, equivalent or molar conductivities may be used. We will prefer the former; the partial equivalent conductances shall be properly noted as mobilities, because they are directly proportional to the velocities of the ions. Putting numerical values for the universal constants entering into formulæ (2) and (5), we find the limiting formula for the mobility of an ion in a simple electrolyte in practical units ( $\text{ohm}^{-1} \text{cm}^2$ ):

$$\left. \begin{aligned} l_j &= l_j^0 - \left( \frac{0.986 \cdot 10^6}{(DT)^{\frac{1}{2}}} w l_j^0 + \frac{29.0 z_j}{(DT)^{\frac{1}{2}} \eta} \right) \sqrt{(z_1 + z_2) \mu} \\ w &= z_1 z_2 \frac{2q}{1 + \sqrt{q}} \\ q &= \frac{\kappa'^2}{\kappa^2} = \frac{z_1 z_2 (l_1^0 + l_2^0)}{(z_1 + z_2)(z_2 l_1^0 + z_1 l_2^0)} \end{aligned} \right\} \quad (8).$$

Here,  $\mu$  means the equivalent concentration,  $z_1, z_2, l_1^0$  and  $l_2^0$  valences and zero concentration mobilities of anions and cations.

The most important difference from the earlier theory is, that in the new theory, the coefficient of the square root term does not contain the ionic radius, so that this coefficient can be computed from the mobilities of the ions present.

For binary electrolytes, formula (8) may be simplified :

$$l_j = l_j^0 - \left( \frac{5.78 \cdot 10^5}{(DT)^{\frac{3}{2}}} z^2 l_j^0 + \frac{29.0 z}{(DT)^{\frac{1}{2}} \eta} \right) \sqrt{2z\mu} \quad (9)$$

We note that this formula contains a law found empirically by Kohlrausch, which states that the mobility of an ion is the same in all

binary electrolytes of the same concentration. However, its validity is restricted to simple binary electrolytes and, even for mixtures of these, deviations are to be expected. Indeed, conductivity measurements performed by Bray and Hunt on mixtures of HCl and NaCl show with certainty, that the rule of independent mobilities does not hold in this case, the deviation being as expected by the theory.

According to our deduction, the limiting formulæ given here should be expected to hold only in the greatest dilutions; when  $l_0 - l$  amounts to 10 per cent. of  $l_0$ , the terms of the second order which we have neglected in the calculation will reach the order of magnitude of 1 per cent.

Investigations on terms of higher order indicate that they should be of opposite sign to that of the square root term in all cases where association in the sense of Bjerrum<sup>3</sup> does not occur. As to association, we should note that it is strongly indicated when the conductivity curves of two electrolytes of the same type show other dissimilarities than would be expected from the differences in the mobilities of the ions and in the viscosities of the solutions. However, it would take us too far too treat this subject further.

4. *Verification by Conductivity Measurements.*—The limiting formula for equivalent conductance may be written simply :

$$\Lambda = \Lambda_0 - \alpha \sqrt{\Gamma},$$

where  $\Gamma$  = twice the ionic strength =  $(z_1 + z_2)\mu$ ;

$$\alpha = \frac{0.986 \times 10^6}{(DT)^{\frac{3}{2}}} \cdot w\Lambda_0 + \frac{29.0}{(DT)^{\frac{1}{2}} \eta} (z_1 + z_2),$$

<sup>3</sup> N. Bjerrum, *Kgl. Danske Vidensk. Selsk. Mat.-fys. Medd.*, VII., 9 (1926).

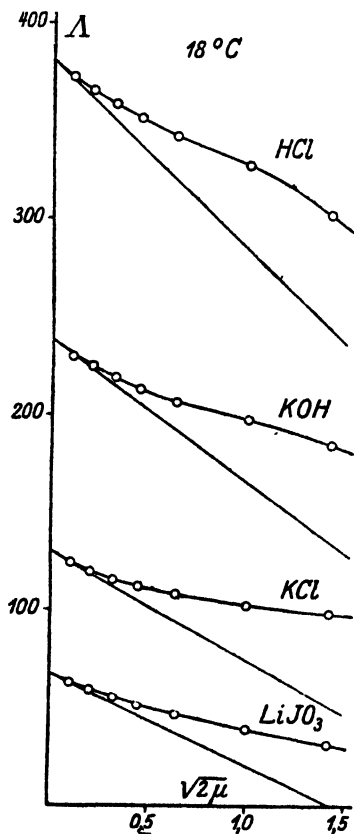


FIG. 1.

$w$  has the value given by (8). When the solvent is water of 18° C., we have :

$$\alpha = 0.270w\Lambda_0 + 17.85(z_1 + z_2).$$

For water at 25° C. :

$$\alpha = 0.274w\Lambda_0 + 21.14(z_1 + z_2).$$

For methanol at 25° C. :

$$\alpha = 1.15w\Lambda_0 + 56.0(z_1 + z_2).$$

Fig. 1 shows the general behaviour of binary monovalent electrolytes in water, the conductivities of four electrolytes being presented as functions of  $\sqrt{2\mu}$ . The slope at zero concentration is given by the simple equation :

$$\alpha = 35.7 + 0.159\Lambda_0.$$

The individual differences of these electrolytes are chiefly given by the limiting slopes, HCl showing the greatest absolute and the smallest relative decrease of  $\Lambda$  with increasing concentration,  $\text{LiIO}_3$  the greatest relative and the smallest absolute decrease. However, in greater concentrations, other influences than that of interionic attraction are quite appreciable, so, for instance when  $\mu > 0.5$ ,  $\text{LiIO}_3$  shows a greater  $\Lambda_0 - \Lambda$  than KCl.

For verification on a larger range of material, we will consider the conductivity measurements of Kohlrausch already adapted by Debye and Hückel, only omitting those salts which are suspect of hydrolysis. From the conductivity values for the greatest dilutions, the coefficients of formula

$$\Lambda = \Lambda_0 - \alpha\sqrt{I} + \beta I$$

have been calculated by the method of least squares. As Debye and Hückel use somewhat different notations, we have partly transformed their figures into our terms.

Table I. gives the  $\alpha$  values ( $\alpha_{\text{exp.}}$ ) calculated in the way described from  $\Lambda$  values at concentrations  $\mu = 0.0001, 0.0002, 0.0005, 0.001, 0.002$ , and  $0.005$ , compared with the  $\alpha_{\text{theor.}}$  computed from  $\Lambda_0$ .

The deviations are within the possible limit of experimental error.

Fig. 2 illustrates the effect of association. As the influence of association, in great dilution, is proportional to the concentration, it does not

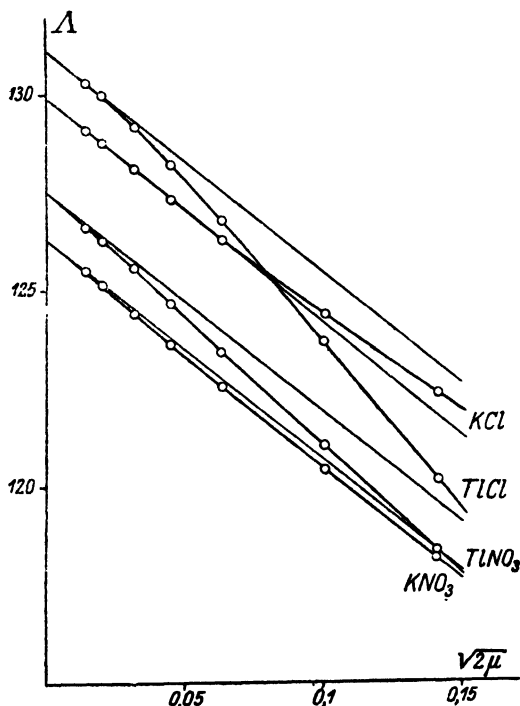


FIG. 2.

TABLE I.

	$\Lambda_0$	$\alpha_{\text{exp.}}$	$\alpha_{\text{theor.}}$	$\alpha_{\text{exp.}} - \alpha_{\text{theor.}}$
LiCl . . . .	98.93	57.35	51.4	6.0
LiIO <sub>3</sub> . . . .	67.35	48.33	46.4	1.9
LiNO <sub>3</sub> . . . .	35.24	56.27	50.9	5.4
NaCl . . . .	108.89	54.69	53.0	1.7
NaIO <sub>3</sub> . . . .	77.42	51.39	48.0	3.4
NaNO <sub>3</sub> . . . .	105.34	58.27	52.5	5.8
KCl . . . .	129.93	59.94	56.4	3.5
KBr . . . .	132.04	62.17	56.7	5.5
KI . . . .	130.52	51.53	56.5	- 5.0
KIO <sub>3</sub> . . . .	98.41	54.18	51.4	2.8
KClO <sub>3</sub> . . . .	119.47	58.16	54.7	3.5
KNO <sub>3</sub> . . . .	126.41	65.67	55.8	9.9
KCNS . . . .	121.04	54.10	55.0	- 0.9
CsCl . . . .	133.08	53.75	56.9	- 3.2
AgNO <sub>3</sub> . . . .	115.82	62.35	54.1	8.3
TlNO <sub>3</sub> . . . .	127.55	63.40	56.0	7.4

affect the limiting slope, which is practically the same for all the four salts considered; with increasing concentration, the individual differences become rather remarkable. However, association to the extent shown by the two thallium salts is not common among uni-univalent salts in water.

Table II. gives the experimental  $\alpha$  values for uni-bivalent salts in water, deduced by Debye and Hückel from the  $\Lambda$  values found by Kohlrausch for  $\mu = 0.0001$ ,  $0.0002$ ,  $0.0005$ ,  $0.001$ , and  $0.002$ ;  $\alpha_{\text{theor.}}$  is given by the equation:

$$\alpha = 53.55 + 1.084 \frac{q}{1 + \sqrt{q}} \Lambda_0;$$

here:

$$q = \frac{\Lambda_0}{\Lambda_0 + l_1},$$

when  $l_1$  is the mobility of the univalent ion.

TABLE II.

	$\Lambda_0$	$\alpha_{\text{exp.}}$	$\alpha_{\text{theor.}}$	Diff.
Ba(NO <sub>3</sub> ) <sub>2</sub> . . . .	116.95	92.8	86.9	+ 5.9
Sr(NO <sub>3</sub> ) <sub>2</sub> . . . .	113.42	97.8	85.5	+ 12.3
CaCl <sub>2</sub> . . . .	116.69	88.0	86.1	+ 1.9
Ca(NO <sub>3</sub> ) <sub>2</sub> . . . .	113.56	97.4	85.6	+ 11.8
MgCl <sub>2</sub> . . . .	110.88	83.2	84.1	- 0.9
K <sub>2</sub> SO <sub>4</sub> . . . .	132.23	81.0	92.1	- 11.1

The deviations from theory are on the whole somewhat greater than for uni-univalent salts, probably for the reason that only five  $\Lambda$  values could be used for the calculation of  $\alpha_{\text{exp.}}$  instead of six values as for the salts in Table I.

Fig. 3 gives the conductivity curves of the uni-bivalent salts. For clarity, some of the curves have been displaced in the figure.

For bivalent binary electrolytes in water  $\alpha_{\text{theor}}$  of the formula :

$$\Lambda = \Lambda_0 - \alpha \sqrt{4\mu}$$

is given by the equation :

$$\alpha = 71.4 + 0.636\Lambda_0.$$

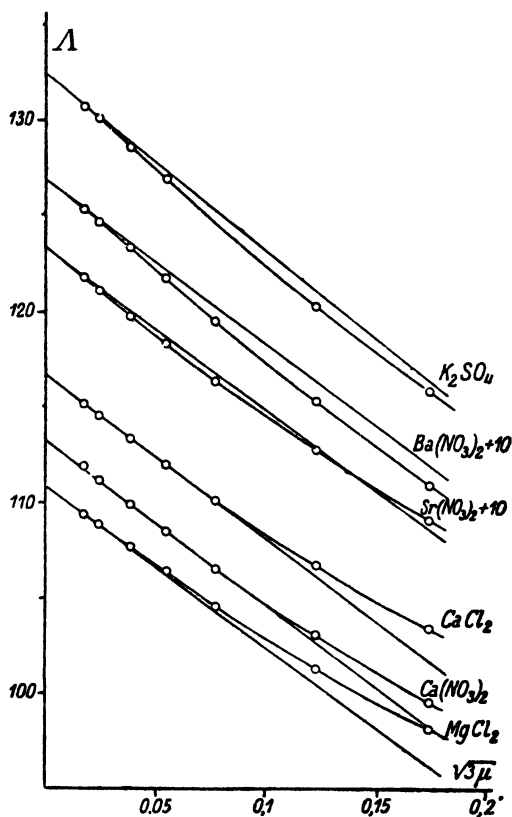


FIG. 3.

Table III is analogous to the former ones,  $\alpha$  and  $\Lambda$  being calculated from the  $\Lambda$  values found for  $\mu = 0.0001, 0.0002, 0.0005, 0.001$  and  $0.002$  by Kohlrausch.

TABLE III.

	$\Lambda_0$	$\alpha_{\text{exp}}$	$\alpha_{\text{theor}}$	Diff.
MgSO <sub>4</sub> . .	114.70	242.7	144.4	98.3
CdSO <sub>4</sub> . .	115.81	270.7	145.1	125.6

The discrepancy is so great that it falls far beyond the limit of experimental error. Debye and Hückel have suggested that the concentrations

may be too great for extrapolation; indeed, the  $\Lambda$  value extrapolated for  $\text{MgSO}_4$  differs considerably from the value 113.10, given by the mobilities of magnesium and sulphate ions, as found from the  $\Lambda$  values of  $\text{MgCl}_2$  and

$\text{K}_2\text{SO}_4$ . Fig. 4 gives the conductivity curve of  $\text{MgSO}_4$ , showing that an extrapolation with the tangent 113.1 - 113.4  $\sqrt{4\mu}$  can be carried out without violation. The extrapolation tangent of Debye and Hückel is also given for comparison.

The rapidly increasing slope indicates an appreciable association; the inversion tangent is given by the dissociation equilibrium.

As regards non-aqueous solutions, we shall consider the measurements of methanolic solutions at 25° C. recently published by Frazer and Hartley. They work on dilutions between  $\mu = 10^{-4}$  and  $\mu = 2 \cdot 10^{-3}$  and find that the square-root formula holds for that range of concentrations. So, they evaluate the measurements graphically,

plotting the  $\Lambda$  values against  $\sqrt{\mu}$  and drawing a straight line. Table IV. gives a comparison between the experimental  $\alpha$  values and the theoretical ones, given by the equation:

$$\alpha = 112 + 0.674\Lambda_0$$

TABLE IV.

	$\Lambda_0$	$\alpha_{\text{exp.}}$	$\alpha_{\text{theor.}}$	$\alpha_{\text{exp.}} - \alpha_{\text{theor.}}$
$\text{LiCl}$ . . . . .	90.90	158	173	- 15
$\text{NaCl}$ . . . . .	96.95	163	177	- 14
$\text{KCl}$ . . . . .	105.05	185	183	+ 2
$\text{RbCl}$ . . . . .	108.65	199	185	+ 14
$\text{CsCl}$ . . . . .	113.60	200	188	+ 12
$\text{KF}$ . . . . .	94.0	167	175	- 8
$\text{KBr}$ . . . . .	109.35	185	186	+ 1
$\text{KI}$ . . . . .	114.85	184	189	+ 5
$\text{NH}_4\text{Cl}$ . . . . .	111.00	187	187	+ 0
$\text{HCl}$ . . . . .	193.5	260	243	+ 17
$\text{LiNO}_3$ . . . . .	100.25	177	180	- 3
$\text{NaNO}_3$ . . . . .	106.45	204	184	+ 20
$\text{KNO}_3$ . . . . .	114.55	244	189	+ 55
$\text{RbNO}_3$ . . . . .	118.15	251	192	+ 59
$\text{CsNO}_3$ . . . . .	122.95	268	195	+ 73
$\text{AgNO}_3$ . . . . .	112.95	319	188	+ 131
$\text{NaBr}$ . . . . .	101.5	170	180	- 10
$\text{NaOCH}_3$ . . . . .	98.40	157	179	- 22
$\text{NaClO}_4$ . . . . .	115.10	198	190	+ 8

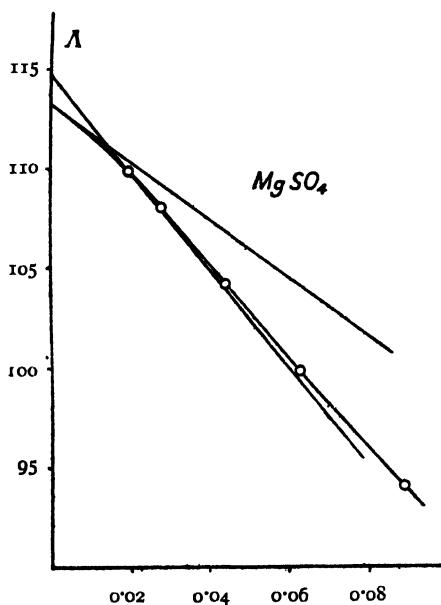
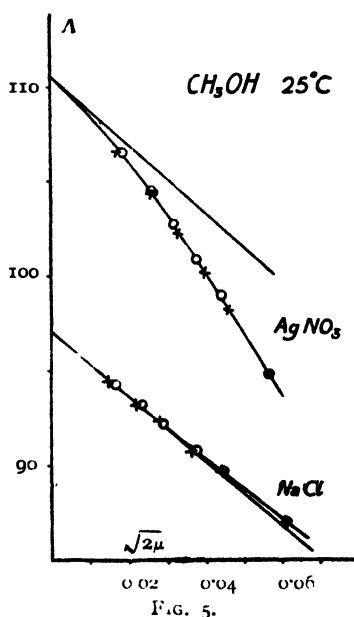


FIG. 4.

Most of the differences are to be considered as real deviations from the limiting law, as no second-order term has been accounted for, and it is probable that most of the electrolytes are associated to a greater or less extent. Fig. 5 shows the conductivity curves of NaCl and AgNO<sub>3</sub> extrapolated according to the theory.

The curve for AgNO<sub>3</sub> shows distinct deviation from a straight line course; it is rather similar to that of TiCl in aqueous solution.

The chief improvement given by the new theory consists in the elimination of all arbitrary constants from the limiting formula. Thus, on one hand, we can put the theory to a much more rigorous test; on the other hand, we can with considerably greater certainty trace and determine other influences than those of the electric forces which the theory involves.



### GENERAL DISCUSSION.

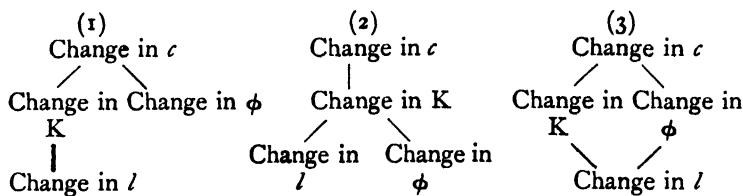
**Mr. H. Hartley** said that the very close agreement between the experimental values and those calculated on Dr. Onsager's theory for uni-univalent and uni-divalent electrolytes in water and for a number of uni-univalent electrolytes in methyl alcohol showed that the new theory accounted satisfactorily for the conductivity of completely dissociated electrolytes in dilute solution in different solvents, and that deviations from the theory, such as those found for di-divalent electrolytes in water and for the nitrates in methyl alcohol, was good evidence of ionic associations or of the formation of complex ions in such cases. Calculations made by Mr. R. P. Bell with the data given in the table on p. 399, indicated that a considerable amount of association or complex ion formation occurred in all solvents other than water and methyl alcohol.

In view of the great experimental difficulties attending the determination of the activities of many solutions of electrolytes the existence of an adequate theory of completely dissociated electrolytes was of much importance to chemists, as the conductivity of a solution could almost always be determined; in conjunction with Dr. Onsager's theory the results would give a valuable clue to its electrical condition.

**Professor T. M. Lowry** asked Dr. Onsager through what range of concentration the deviations he had mentioned extended.

**Professor Allmand** asked whether Dr. Onsager or others could throw light on the following points. (1) What was the nature of the relation between the mobility of an ion in a solution of appreciable concentration (free from non-electrolytes) and the actual macroscopic viscosity of the solution?

By which, if any, of the following schemes, could the relation be qualitatively expressed? [Concentration  $c$ ; fluidity  $\phi$ ; ionic mobility  $l$ ; forces acting on ion (interionic and electrophoretic considered together)  $K$ .]



Schemes (1) and (2) would mean that ionic mobility was determined solely by considerations arising out of the Debye-Hückel-Onsager theory and that, leaving out of consideration cases of *negative* viscosity, the increase in macro-viscosity due to increased ionic concentration had no direct influence on ionic mobility. In other words if the Stokes' equation, in its simplest or in a modified form, be applied to the movement of an ion, the viscosity entering would *always* be the viscosity of the liquid medium, free from ions. Scheme (2) would indicate, in addition, that the increase in viscosity due to increase in ionic concentration, as usually measured, was governed by the same factors as entered into the Debye-Hückel-Onsager theory. Some mechanism involving preferential adsorption of ions of one sign on the walls of the viscosimeter might be imagined. On the other hand, scheme (3) would indicate the necessity of applying a so-called viscosity correction (Sutherland; Bousfield and Lowry; Washburn) to experimental mobilities before the latter could be compared with the values calculated by applying the considerations of Debye, Huckel, and Onsager.

(2) In considering the diffusion coefficients of aqueous electrolytes of *finite* concentration from the point of view of the Nernst formula ( $D = RT \times \frac{2UV}{U + V}$ ), it would appear necessary (a) to introduce the osmotic coefficient (b) to use, not mobilities at infinite dilution, but actual "true" mobilities holding for the given concentration conditions. Would these mobilities be the same as those determined by conductivity and true transference number measurements? Or would they perhaps be *greater*? For it appeared to the speaker that the Debye-Hückel electrophoretic retarding effect, which, according to the authors of the theory, could be regarded as the action on the movement of the ions of a stream of solvent molecules carried in the opposite direction by ions of opposite charge, would not be operative in cases of diffusion. Diffusion measurements made by Öholm and in his own laboratory appeared to indicate that, whilst the concentration at which minimum values of  $D$  occurred could be calculated by the above type of formula for solutions of KCl, NaCl and LiCl, the experimental values of the diffusion coefficients at finite concentrations were always greater than the calculated figures; the discrepancy might disappear if the correct mobilities to use were greater than the ordinary "true" mobilities.

Mr. C. R. Bury expressed doubt whether Stokes' law were applicable to bodies as small as ions. Millikan had investigated its applicability for small particles during the course of his researches on the charge of an electron, and had expressed the opinion that Stokes' law can only be regarded as valid, in liquids, for spheres of radii greater than  $10^{-6}$  cm. Most ions were considerably smaller than this, and radii deduced for them

by Stokes' law were smaller than their true radii. This probably accounted for the inconsistency of the figures for the degree of hydration of ions obtained by Professors Remy and Ulich, and commented on by Professor Allmand; and also for the fact that Messrs. Hartley and Raikes found some ions in solution to be smaller than the corresponding ions in crystals.

**The President** asked if Dr. Onsager could indicate, for the benefit of those chemists who were not familiar with the mathematical treatment of this subject, in what way the properties of the solution deviated from those represented by the formulæ, when the concentration became greater than  $N/100$ , or whatever the limit of their application might be. For instance, was it the viscosity or some other property of the solution which changed in an unknown way as the concentration was increased? Practical chemists were chiefly interested in solutions of fairly high concentration, and it would be of interest to know what was the physical meaning of the deviations from theory which were found to occur.

**Mr. C. W. Davies** (*communicated 12th May, 1927*). **The Extent of Dissociation of Salts in Water.** The equivalent conductivity of an electrolyte changes with increasing concentration of the solution; in general, this change is due to two factors, to the decrease in ionisation of the solute and to changes in the mobilities of the ions.

In a sufficiently dilute solution the second of these two effects alone will persist and there will be a region in which the solute can be regarded as completely dissociated. The concentration at which this will no longer be the case will depend on the character of both solute and solvent. For the inorganic salts in liquid ammonia or acetone (Dielectric Constant *ca.* 22) the effect of incomplete ionisation appears to become apparent below  $10^{-4}$  equivalents per litre. In water (D.C. 81) we have "weak" electrolytes—phosphoric acid, magnesium oxalate,—where this region is not realisable by experiment; "intermediate" electrolytes such as iodic acid (whose dissociation constant  $K = 0.17$ ), which can be regarded as completely ionised at  $0.001N$ ;<sup>1</sup> and "strong" electrolytes—the uni-univalent salts. These latter can be regarded as completely dissociated up to much higher concentrations than  $0.001N$ , but in moderately concentrated solutions it is to be anticipated that the effect of incomplete ionisation will no longer be negligible.

This point has been emphasised in the papers of Onsager<sup>2</sup> and MacInnes and Cowperthwaite,<sup>3</sup> and in view of their work it seems to deserve closer consideration than it has yet had.

The extent of dissociation of bi-bivalent salts will first be considered and the uni-univalent salts will then be briefly discussed. No quantitative treatment of salts of mixed valence types has been attempted since uncertainty as to the character and mobility of possible intermediate ions would render the results of little value.

In discussing incompletely dissociated substances it is necessary to distinguish between the activity coefficient,  $\gamma$ , defined by the equation

$\gamma = \frac{a_{\pm}}{m}$  (where  $a_{\pm}$  is the mean ion activity and  $m$  the molality of the solution); and the quantity  $f_{\pm} = \sqrt{f_c \cdot f_a}$ , which will be called the mean ion-activity-coefficient and is defined by the equation:  $f_{\pm} \cdot m_i = a_{\pm}$ ,

or 
$$\gamma = \frac{f_{\pm} \cdot m_i}{m} \quad . \quad . \quad . \quad . \quad . \quad (I)$$

<sup>1</sup> *J. physical Chem.*, **29**, 986 (1925).

<sup>2</sup> See p. 341.

<sup>3</sup> See p. 400.

$m_i$  being the concentration of ionised molecules in moles per 1000 g. of water (or, in dilute solutions, in moles per litre). This ion-activity-coefficient represents the effect of inter-ionic attraction whereas the stoichiometric activity coefficient involves both this and the degree of dissociation.

*Bi-bivalent Salts.*—The equation of Onsager connecting the mobility of an ion with the ion-concentration is, for the majority of electrolytes in water, in striking agreement with the experimental data. In the case of magnesium sulphate, however,—and the same applies to other bi-bivalent salts—the actual decrease in conductivity is greater than that predicted by the theory. This discrepancy is most readily explained by supposing the salt to be incompletely dissociated.

The Onsager equation for a bi-bivalent electrolyte in water at 18° is:—

$$\Lambda_x = \Lambda_0 - (142.8 + 1.272\Lambda_0)\sqrt{C_i} \quad . \quad . \quad (2)$$

where  $\Lambda_x$  is the sum of the mobilities of cation and anion in a solution in which the equivalent concentration of ions is  $C_i$ . If this equation is provisionally adopted, it is possible to calculate from the conductivity data the concentrations and the activities of the ions at each concentration.<sup>4</sup>

Let  $\Lambda$  be the equivalent conductivity of a salt at total equivalent concentration  $C$ , and let  $C_i$  be the concentration of ions present in the solution. The degree of dissociation is given by the ratio  $\frac{\Lambda}{\Lambda_x} = \frac{C_i}{C}$ . Combining this with equation 2 gives:—

$$\Lambda_x = \frac{\Lambda \cdot C}{C_i} = \Lambda_0 - (142.8 + 1.272\Lambda_0)\sqrt{C_i} \quad . \quad . \quad (3)$$

From this equation it is possible by a short series of approximations to calculate  $C_i$  and, by subtraction,  $C_u$ , the equivalent concentration of undissociated molecules.

For a bi-bivalent electrolyte the mass action expression is:—

$$\frac{C_i^2 f_c \cdot f_a}{2 \cdot C_u \cdot f_u} = K \quad . \quad . \quad . \quad (4)$$

where  $K$  is the true dissociation constant, and  $f_u$ —the activity coefficient of the unionised fraction—may be taken as equal to unity in very dilute solutions. The factor 2 is introduced into the denominator to convert the equivalent into molar concentrations. The ratio  $\frac{K}{f_c \cdot f_a} = \frac{C_i^2}{2C_u} = K'$  can therefore be calculated. To obtain  $K$ , use is made of the well-known limiting equation:  $\log \gamma = -A\sqrt{C}$ , which has been found to hold for all electrolytes hitherto examined up to a concentration of approximately 0.01  $N$ . In the present case this becomes:  $\log f_c \cdot f_a = -2A\sqrt{C_i}$ . If therefore  $\log K'$  is plotted against  $\sqrt{C_i}$  a straight line is obtained which determines the values of  $K$  and  $A$ .

The results of the calculation for  $MgSO_4$  are plotted in the figure. In this case there is some uncertainty as to the  $\Lambda_0$  value, since the mobilities of  $Mg^{++}$  and  $SO_4^{--}$  at infinite dilution are not known with great accuracy.

<sup>4</sup> The method of calculation is that introduced by the writer in discussing weak uni-univalent electrolytes. (*J. physical Chem.*, **29**, 973, 1925; and *Phil. Mag.*, 1927); Sherrill and Noyes (*J. Am. Chem. Soc.*, **48**, 1861, 1926) and MacInnes (*ibid.*, **48**, 2068, 1926), have employed a similar method of treatment which, however, involves an additional assumption as to the validity of the Debye-Hückel limiting activity equation.

The probable value obtained from conductivity data is 113.4 and the calculations have been made for this value and for several other values lying in this neighbourhood. From the figure it will be seen that the value  $\Lambda_0 = 113.5$  gives the best straight line and this yields the result:  $K = 0.00612$ ;  $A = 3.66$ .

These values may be regarded with suspicion as depending on the selection of the most appropriate  $\Lambda_0$  value as well as on the validity of the

Onsager equation; but they can be checked to some extent by freezing-point measurements in the following way.

The Onsager limiting equation breaks down at about  $0.02 N$ , but once the value of  $K$  has been determined, the ion concentrations, activity coefficients and mobilities at the higher concentrations can be obtained from the results of activity measurements.

From the equation  $\gamma^2 m^2 = a_2 K$  the value of  $a_2$  is calculated and, if this is assumed to be equal to  $m_{\pm}$ ,  $m_i$  and consequently  $f_{\pm}$  and  $\Lambda_x$  are obtained.

The validity of the assumption that the activity is equal to the concentration for the undissociated molecules is, of course, uncertain. It seems to be justifiable up to an ion concentration of  $0.1 N$ , but at higher concentrations the activity is probably appreciably greater than the concentration.

The results of this treatment are illustrated for  $MgSO_4$  in Table I., where the activity values are those obtained by Lewis and Randall<sup>5</sup> from the freezing-point measurements of Hausrath and others.

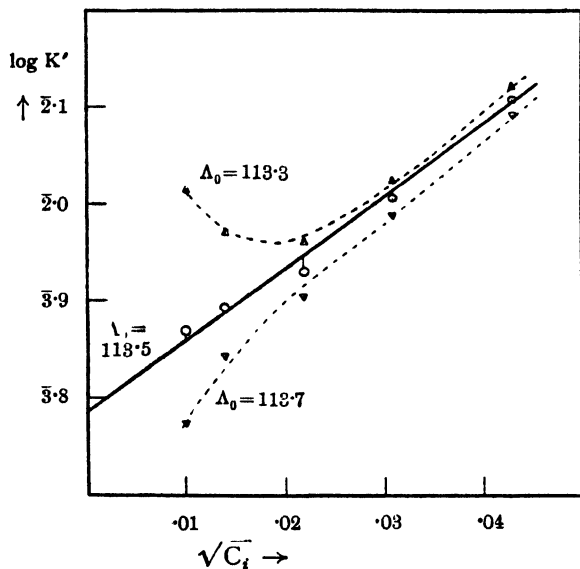


FIG. 1.— $MgSO_4$ .

TABLE I.

$MgSO_4$ .

$K = 0.00612$ .

$m$ .	$\gamma$ .	$a_2$	$C_i$ .	$C_i$ (cond).	$f_{\pm}$ .
0.001	.85	0.000012	0.00198	0.001975	.86
0.002	.81	0.000043	0.003914	—	.83
0.005	.75	0.00023	0.00954	0.009535	.79
.001	.69	0.00078	0.01844	0.01864	.75
.002	.61	0.0024	0.0352	—	.69
.005	.50	0.010	0.080	—	.63
.01	.404	0.0267	0.1466	—	.55
.02	.321	0.0673	0.2654	—	.48
.05	.225	0.207	0.586	—	.38
.1	.160	0.450	1.10	—	.30

<sup>5</sup> Lewis and Randall, "Thermodynamics," p. 344 (1923).

In column 5 are given the ion concentration values obtained from the conductivity data by the former method of calculation. They agree well with the values in column 4.

Conductivity data are also available for  $\text{ZnSO}_4$ ,  $\text{CdSO}_4$ ,  $\text{CuSO}_4$ , and  $\text{MgC}_2\text{O}_4$ , and these salts have been treated in the same way as  $\text{MgSO}_4$ . Curves similar to those shown were obtained in each case, and the results are shown in Table II.

TABLE II.

Salt.	$\Lambda_0$ .	K.	A.
$\text{MgSO}_4$	113.50	0.0061	3.7
$\text{ZnSO}_4$	113.50	0.0045	3.7
$\text{CdSO}_4$	113.90	0.0038	3.5
$\text{CuSO}_4$	113.85	0.0045	3.3
$\text{MgC}_2\text{O}_4$	107.00	0.00037	3.5

\* Magnesium sulphate is the strongest of these electrolytes, but its dissociation constant is no greater than that of o-nitro-benzoic acid ( $K = 0.0062$  at  $25^\circ$ ). The weakest, magnesium oxalate, is more comparable with formic acid.

The  $\Lambda$  values are more uncertain, as is evident from an inspection of the figure, since they depend so largely on the values adopted for  $\Lambda_0$  and on the accuracy of the conductivity data at extreme dilutions. They are all larger than the value given by the Debye-Hückel theory, which for a bi-valent electrolyte is 2.81.

*Uni-Univalent Salts.*—The dissociation constants of the uni-univalent salts are much larger than those of the bivalent electrolytes, and the unionised fraction only becomes measurable in more concentrated solutions where the Onsager equation is inapplicable and where the conductivity data are subject to a viscosity correction. Still, approximate values for the extent of ionisation of the common salts seem likely to be of interest, and the figures of MacInnes and Cowperthwaite<sup>8</sup> provide a starting-point. These writers find that hydrogen, lithium, sodium and potassium chlorides in 0.1 *N* solution are completely dissociated, so that in these five electrolytes the mobility changes are not masked by the effect of incomplete dissociation.

Now the Onsager equation for uni-univalent electrolytes:

$$\Lambda = \Lambda_0 - (50.49 + 0.2238\Lambda_0)\sqrt{c}$$

only holds up to a concentration of 0.002; but it has been found that for the chlorides mentioned the deviations from this equation at the higher concentrations are larger the larger the  $\Lambda_0$  value; and that, in fact, the equation,

$$\frac{\Lambda_0 - \Lambda \cdot \eta^5}{(50.49 + 0.2238\Lambda_0)} = f(c) \quad (5)$$

is approximately true for these electrolytes and some others even up to concentrations of 0.5 *N* and beyond. The values found for  $f(c)$  are given in the following table:

C =	.005	.01	.02	.05	.1	.2	.5
$f(c)$	.07006	.09441	.1246	.1748	.2239	.2789	.3548.

In the equation  $\eta$  is the relative viscosity of the solution. This viscosity correction is, of course, purely empirical; it is the one which gave the best

average agreement for the electrolytes examined. Actually the true viscosity correction is most uncertain and probably varies from ion to ion: this is certainly the chief, if not the only difficulty in the accurate extension of the limiting equation into higher concentrations.

Equation 5 has been applied to the uni-univalent electrolytes quoted by Noyes and Falk<sup>6</sup> in their valuable collection of the data. For six salts the agreement up to 0.5 *N* is good, the maximum deviation being 0.4 per cent. (the viscosity correction is in some cases ten times this amount), and these salts are presumed to be completely dissociated. They are: lithium, sodium and potassium chlorides, potassium bromide, potassium thiocyanate and lithium nitrate. For the remainder, the experimental conductivity figures at the higher concentrations become in every case lower than the calculated, and the ratio  $\Lambda^{\text{exp.}}/\Lambda^{\text{calc.}}$  is taken as an approximate measure of the degree of dissociation. The dissociation constants can then be calculated, assuming, as before, that  $c(1 - \Lambda^{\text{exp.}}/\Lambda^{\text{calc.}}) = a_2$ , and introducing this value into the equation  $\gamma^{2m^2}/a_2 = K$  where  $\gamma$  is the experimentally determined stoichiometric activity coefficient. The results are shown in Table III., the activity coefficients being again taken from Lewis and Randall<sup>5</sup> except in the cases specially noted.  $\Lambda/\Lambda_x$  represents the degree of ionisation and *K* the dissociation constant derived.

TABLE III.

	C =	'01.	'02.	'05.	'1.	'5.
Sodium Nitrate*	$\Lambda/\Lambda_x$	—	—	'991	'985	—
	<i>K</i>	—	—	3'85	3'86	—
Potassium Nitrate	$\gamma$	'916	'878	'806	'732	—
	$\Lambda/\Lambda_x$	'994	'989	'975	'961	—
	<i>K</i>	1'40	1'38	1'32	1'37	—
Silver Nitrate	$\gamma$	'902	'857	'783	'723	'526
	$\Lambda/\Lambda_x$	'993	'989	'973	'957	'883
	<i>K</i>	1'10	1'31	1'12	1'23	1'18
Thallous Nitrate*	$\Lambda/\Lambda_x$	'984	—	'946	'917	—
	<i>K</i>	'521	—	'573	'591	—
Sodium Iodate	$\gamma$	—	'840	'765	'692	—
	$\Lambda/\Lambda_x$	—	'996	'988	'984	—
	<i>K</i>	—	3'44	2'42	3'00	—
Potassium Iodate	$\gamma$	'882	'840	'765	'692	—
	$\Lambda/\Lambda_x$	'997	'994	'984	'976	—
	<i>K</i>	2'99	2'30	1'85	2'00	—
Potassium Chlorate*	$\Lambda/\Lambda_x$	'994	'989	'977	'968	—
	<i>K</i>	1'40	1'44	1'42	1'70	—
Potassium Bromate*	$\Lambda/\Lambda_x$	—	'993	'984	'977	—
	<i>K</i>	—	2'25	2'03	2'41	—
Thallous Chloride†	$\Lambda/\Lambda_x$	'972	—	—	—	—
	<i>K</i>	0'300	—	—	—	—
Rubidium Chloride†	$\Lambda/\Lambda_x$	—	—	—	'990	—
	<i>K</i>	—	—	—	5'88	—
Caesium Chloride†	$\Lambda/\Lambda_x$	—	—	—	'981	—
	<i>K</i>	—	—	—	3'18	—

The constancy of these rather tentative *K* values is good in view of the enormous effect upon  $a_2$  of small errors in  $\Lambda_0$  or in the derivation of  $\Lambda^{\text{calc.}}$

Of the other electrolytes examined, lithium iodate begins to show the

\* Assuming that the ion-activity-coefficient is the same as that of potassium nitrate at the same concentration.

† Assuming that the ion-activity-coefficient is the same as that of potassium chloride.

<sup>6</sup> *J. Amer. Chem. Soc.*, 34, 461 (1912).

effect of incomplete dissociation at 0.1  $N$ ; its strength is approximately the same as that of rubidium chloride but cannot be safely calculated owing to the magnitude in this case of the viscosity correction. The strength of the fluorides and of the acids also could not be calculated owing to the absence of viscosity data.

For the salts that have been examined it will be seen, that salts containing a common anion fall, in strength, in the following order:



and that the dissociation constants of those containing a common cation decrease in the order  $\text{Cl} > \text{IO}_3 > \text{BrO}_3 > \text{ClO}_3, \text{NO}_3$ . Thallous chloride is an apparent exception.

**Dr. Onsager** replied that the theory accounted for the influence of Coulomb's forces upon the mobilities of the ions. The square root formula was only an approximation, applicable in great dilutions. At finite concentrations deviations from that formula must necessarily occur even if no other effects at all were operating. The deviations from the square root law would depend upon the individual properties of the ions, such as the dimensions of the ions, the variation of viscosity with concentration and, particularly, upon the deviations from Coulomb's law which would probably occur when the distance between two ions became small ("association" and "hydration").<sup>7</sup>

In the conductivity theory no attempt had been made to improve the simplified mathematical treatment of Coulomb's forces which led to the square root law. However, in the thermodynamic theory such advances had been made. Besides Professor Bjerrum's investigation<sup>8</sup> attention should be drawn to the recent papers of Gronwall<sup>9</sup> and Müller.<sup>10</sup>

As to Professor Allmand's question regarding viscosity, his scheme (3) was essentially the right one; however, at greater concentrations the effects of interionic forces and viscosity would interfere with each other to a certain extent. There was some uncertainty about the viscosity correction even for dilute solutions; firstly, because the ions could not be expected to obey Stokes' law exactly; secondly, because the composition of the solution surrounding an ion would differ from that of the solution in bulk. Though the viscosity correction should of course be taken into consideration for the interpretation of the conductivity curves, it was of minor importance for the testing of the theory, as the deviations from the limiting formula would in general depend more upon the other individual properties of the electrolytes.

As to the question regarding diffusion, the activity coefficients should be introduced as had been done by Schreiner.<sup>11</sup> The mobilities should always be taken as greater than those obtained from the conductance data. Schreiner took the limiting mobilities; this was approximately right for simple electrolytes when there was no diffusion potential and the viscosity correction was negligible. For simple electrolytes, the diffusion coefficient would not be influenced by the effect he (Dr. Onsager) had described as "ionic forces," because both kinds of ions migrated with the same velocity in the same direction, and need not pass each other. The electrophoresis effect would be zero when there was no diffusion potential, and negligible for binary electrolytes, when the transference member did not differ much from 0.5.

<sup>7</sup> The question has been discussed more extensively in *Physik. Z.*, 1927, 28, 277-298.

<sup>8</sup> *Kgl. Danske Vidensk. Selsk., Mat. fys. Medd.*, 7, 9, 1926.

*Proc. Amer. Nat. Acad. Scient.*, April, 1927.

*Physik. Z.*, 1927, 28, 324.

<sup>11</sup> *Tidsskrift for kemi og bergvaesen*, 1924.

# REFRACTOMETRIC EVIDENCE FOR THE EXISTENCE OF UNDISSOCIATED MOLECULES AND COMPLEX IONS IN SOLUTIONS OF STRONG ELECTROLYTES.

BY K. FAJANS.\*

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## 1. Introduction.

On the basis of the investigations of recent years we may regard as certain the conclusion that the union of ions whether to form molecules of a gas, or complex ions, or crystals, is always accompanied by a more or less extensive change in the properties of the ions themselves.<sup>1</sup> This conclusion is to be drawn above all from the molecular refractivity, which upon the union of the ions shows systematic deviations from strict additivity,<sup>2</sup> as well as from changes in the absorption of light,<sup>3</sup> from the inconstancy of the active radii of the ions in crystal lattices<sup>4</sup> and from other considerations. In this paper we shall give an account of an attempt to obtain from this knowledge some light on the behaviour of the ions in solutions of salts.

The conclusions drawn are on the whole independent of the particular theoretical significance attached to the above-mentioned changes in the ions. Yet the exposition of the relationships involved is very much facilitated by the use of a conception which has already shown itself serviceable in many respects. We shall regard these changes in the properties of an ion as due to its polarisation, or to a deformation of its electron shells, under the influence of the electric fields of neighbouring ions.

Here we must emphasise that by polarisation or deformation we are to understand not only the production of dipoles by electrostatic induction such as occurs when two ions unite to form a free molecule,<sup>5</sup> but also the polarisation possessing higher degrees of symmetry which an ion forming part of a crystal lattice suffers, due to the action of the several other ions surrounding it at different points.

This mutual action of the ions on each other is very strongly dependent upon the interionic distance, as is shown by the well-known dependence of the colour of many salt-like compounds upon the temperature. If AgBr at ordinary temperatures is yellow, but colourless at the temperature of liquid air, this obviously means that, due to the increase in the amplitude of the vibrations of the ions in the lattice with increasing temperature, the centres of the ions approach each other more closely from time to time, thus exposing their electronic systems to stronger electric fields.

\* Translated from the German by O. Koenig.

<sup>1</sup> Fajans, *Naturwiss.*, 1923, 11, 165; later cited as I. *Z. Kristall.*, 1925, 61, 18; "Progress of the Physical Sciences" (Russian), 1926, 5, 294, cf. also the article of Grimm in Geiger-Scheel, *Handbuch der Phys.*, 1927, Vol. 24, especially pp. 479 and 561 and of Born, *ibid.*

<sup>2</sup> Fajans and Joos, *Z. Physik.*, 1924, 23, 1; Fajans and Knorr, *Ber.*, 1926, 59, 249.

<sup>3</sup> Meisenheimer, *Z. physik. Chem.*, 1921, 97, 304; Fajans, Halban and Ebert, *Z. physik. Chem.*, 1924, 112, 321; Scheibe, *Ber.*, 1926, 59, 1321, 2617; Hantzsch, *ibid.*, p. 1096.

<sup>4</sup> Fajans; Goldschmidt, *Norske Videnskaps-Akad.*, 1926, Nos. 2 and 8.

<sup>5</sup> Born and Heisenberg, *Z. Physik.*, 1924, 23, 388.

It is now quite permissible to enlist the aid of these experimentally determinable changes, in order to answer the question, whether the ions in solutions of strong electrolytes can approach as closely to each other as they do in gaseous molecules or in crystals, that is, whether the distance separating oppositely charged ions can become so small, that there is no molecule of the solvent present between them. This question is on the one hand very closely related to the possibility of the existence of undissociated molecules and complex ions in solutions of strong electrolytes, to which recently valuable contributions have been made.<sup>6</sup> On the other hand it touches directly upon one very important point in the theory of Debye and Hückel which is so successful in many respects. As we know, in order to give an account of the characteristic behaviour of the individual electrolytes at finite concentrations, there was introduced into this theory a parameter having the dimension of length, which is supposed to give the value of the smallest distance to which the ions in the solution can approach each other. But contrary to expectation one obtains values, for instance for the alkali chlorides, which show the following sequence :<sup>7</sup>



which is exactly the reverse of the sequence to be expected on the basis of the lattice distances. This discrepancy, moreover, was not removed by the further development of the theory by Hückel<sup>8</sup> (taking into account the change in the dielectric constant) or by Bjerrum<sup>9</sup> by introduction of the idea of the "association" of ions. These oppositely directed sequences of the ionic radii in the solution and in the crystal respectively could possess a real meaning only provided that, even when the ions in solution approach each other as closely as possible, water molecules still remain between them: for  $\text{Li}^+$  certainly holds the water more strongly than  $\text{Cs}^+$ .

When in the following pages, use is made of the expression "relative magnitudes" of the ions, we shall mean not the gradations in magnitude resulting from the theory of Debye and Hückel, but rather those obtained on the basis of the atomic structures and the lattice distances.<sup>10</sup>

## 2. General Remarks on the Changes of Refractivity of the Ions in Crystals.

The quantitative study of the refraction and the absorption of light by the solutions will be particularly suited to the answering of the above question. The purpose of this paper is to give an account of the dependence of the refractivity upon the concentration, for solutions of a series of salts, an investigation which has already yielded valuable insight into these relationships.

All further conclusions are based upon the assumption that the Lorentz—Lorenz expression for the refractivity,  $R$ , namely

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{G}{d}$$

<sup>6</sup> Cf. the references to the literature in Section 9 and the discussion of this question by Bjerrum, *Erg.-exakt. Naturwiss.*, 1926, 5, 139; further Drucker and Riethof, *Z. physik. Chem.*, 1924, 111, 1.

<sup>7</sup> Hückel, *Erg. exakt. Naturwiss.*, 1924, 3, 221.

<sup>8</sup> Hückel, *Physik. Z.*, 1925, 26, 93.

<sup>9</sup> *Danske Videnskab. Selskab.*, 1926, VII., 9.

<sup>10</sup> Cf. Grimm, *Handbuch der Physik.*, 1926, 22, 499; Goldschmidt, *loc. cit.*

(where  $n$  is the refractive index,  $d$  the density, and  $G$  the weight), can be calculated, for a system of several components, in a strictly additive manner from the individual refractivities of these components, provided that the electronic systems of the components remain unchanged in the mixture. Every deviation from additivity is thus to be regarded as an indication of influences exerted by the components in question upon each other.

We can see an argument for the expediency of this assumption on the one hand in the fact that, as will be shown in Section 6, the additivity found by A. Heydweiler<sup>11</sup> for the refractivity of salt solutions at infinite dilution (in which state the ions exert no forces upon each other), is found to hold even when the accuracy of the measurements is considerably increased. On the other hand, as was shown by Fajans and G. Joos, the marked deviations from additivity which accompany the transition, from the state of infinite dilution, to the crystal or to the molecule, show regularities of such simplicity and theoretical plausibility that one can hardly doubt that they are, at least to a certain extent, an expression of the mutual influences between the ions proper, or between the ions and the solvent. In consideration of the importance of these conclusions for what follows, we may here summarise some of the results obtained with Joos.

The examination of a large amount of experimental material showed the following propositions (from which to date no certain exceptions have been found), to be valid.

The refractivity of the anions is lowered by neighbouring cations, and lowered the more, as the electric field of the cation is stronger (*i.e.*, as its radius<sup>12</sup> is less and its charge greater), and as the anion is more polarisable (*i.e.*, more deformable). It is the refractivity itself (strictly only for infinitely long waves)<sup>13</sup> which, on the basis of the theory of Lorentz, serves in the comparison of analogous ions as a measure of the polarisability.

The refractivity of the cations is increased by neighbouring anions. The magnitude of the increase here depends upon the field strength (charge and radius) of the anion, and upon the polarisability (*i.e.*, the refractivity) of the cation.

These regularities are easily understood when one considers that the refractivity of an ion is a measure of its polarisability, that is, of the ease of displacement of its electron shells with respect to its nucleus. The refractivity of an anion must consequently sink, when to the attractive action of its own nucleus upon its electron shells, there is added that of a neighbouring positively charged cation. Anions are thus rendered more rigid—consolidated—by cations. Inversely the electron shells of a cation suffer a repulsion at the hands of the neighbouring anions, the cation is rendered less rigid, its refractivity rises.<sup>14</sup>

The union of ions into molecules or crystals will thus be accompanied by a net diminution of the refractivity whenever the consolidating effect of the cation upon the anion outweighs the loosening effect of the anion upon the cation, and *vice versa*.

The relationships are particularly simple in the case of the alkali halides. Here all the ions bear unit charge, and the ionic radii as well as the ionic

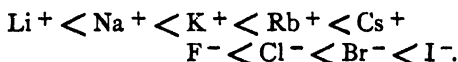
<sup>11</sup> *Physik. Z.*, 1925, 26, 526.

<sup>12</sup> The structure of the outermost electron shell of the cation is also of decisive importance, but since we shall here consider only cations possessing the structure of the inert gases of the zero group, this point need not be further discussed.

<sup>13</sup> All the refractivity values in this communication are for the D-line and differ but slightly from those for infinitely long waves.

<sup>14</sup> Cf. also Herzfeld and Wolf, *Ann. Physik.*, 1925, 78, 35, 195.

refractivities vary from ion to ion in a parallel way, that is, the following series hold good both for radius and for deformability :



At the same time it follows, on the basis of the resolution of the experimentally found refractivities of the salts into values for the individual cations and anions (as carried out by Wasastjerna,<sup>15</sup> and by Fajans and Joos), that the refractivities of  $\text{F}^-$  and  $\text{K}^+$  are approximately equal. Similar relationships hold for the ionic radii. Fig. 1 in which the values of  $R_{\text{solid}} - R_{\text{free ions}}$  are plotted is now comprehensible. In the case of additivity all the values of this function would have to be equal to zero. But as Spangenberg<sup>16</sup> has shown, the solid alkali halides do not fulfil the condition of additivity and, in the figure, one obtains for the majority of the salts a negative value, that is, a net consolidation, upon formation of

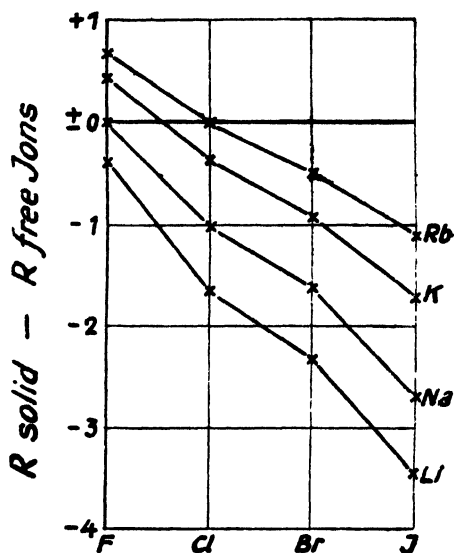


FIG. 1.

the crystal from the free ions since the cations are in general smaller and less deformable than the anions. Only in the case of  $\text{KF}$  and  $\text{RbF}$ , where the smallest anion is united with the largest cations, does the loosening effect of the anion upon the cation predominate, thus resulting in an increase of refractivity upon formation of the crystal lattice from the free ions.

There is one more peculiarity in the behaviour of the cations and anions in the lattice which deserves to be mentioned, because we shall find it to recur for solutions. The value zero for the function  $R_{\text{solid}} - R_{\text{free ions}}$  means that the opposite effects of the two ions upon each other just cancel out. On the assumption that the effect in any

given case depends upon the field strength of the ion exerting the deforming action and upon the polarisability of its partner, one would expect to find the closest approximation to the value zero in that alkali halide, in which cation and anion are the most nearly alike as regards radius and refractivity, that is, in  $\text{KF}$ . As a matter of fact, however, for  $\text{KF}$  the available measurements (whose accuracy might well be improved), show a distinct increase in refractivity accompanying the union of the ions into the crystal; the value nearly zero on the other hand appears for  $\text{NaF}$  and for  $\text{RbCl}$ , in which salts the anion is decidedly larger and more deformable than the cation. From this it seems that for conditions of equal radius and deformability, the influence of the anion upon the cation is greater than the opposite effect.

<sup>15</sup> *Z. physik. Chem.*, 1922, 101, 193; *Soc. Scient. Fennica*, 1923, I., 37, 38.

<sup>16</sup> *Z. Kristall.*, 1923, 57, 494.

### 3. Influence of the Ions upon the Refractivity of Water.

We must call attention to another point which is of great importance for what follows. We must distinguish between the value of the refractivity of an ion in infinitely dilute solution, and the value which would be found were the ion in the free gaseous state.<sup>17</sup> For a cation, just as it diminishes the refractivity of a neighbouring anion, will in like manner diminish that of the water surrounding it in solution, whereas an anion should have a loosening effect upon the water. This effect is considerable only in the case of very small or highly charged ions, for the deformability of water is small, as is shown by its low molal refractivity (3.71 as against 9.00 for  $\text{Cl}^-$  or 19.24 for  $\text{I}^-$ ). By means of this effect the following at first sight very peculiar fact is explained.

If one calculates the refractivity of, for example,  $\text{AlCl}_3$ , in extremely dilute solution, in the usual manner, that is by subtracting from the refractivity of the solution that of the water, assuming the latter to be unchanged by the presence of the solute, one obtains the value 24.6. Now the three  $\text{Cl}^-$  ions have a refractivity value of  $3 \times 9.00 = 27.0$ .<sup>18</sup> For the dissolved  $\text{Al}^{+++}$  there thus results the physically nonsensical negative value of  $24.6 - 27.0 = -2.4$ . Since free gaseous  $\text{Al}^{+++}$  must have a value of about +0.17, the anomaly can only be understood on the supposition that too much has been subtracted from the total refractivity of the solution in taking account of the water, *i.e.*, that the latter's refractivity had actually been greatly decreased by the strong field of the small and highly charged  $\text{Al}^{+++}$  ion. Of course this decrease is distributed among the several water molecules surrounding the  $\text{Al}^{+++}$  ion in the dilute solution. Likewise in the case of several other ions important for what follows, an influence upon the refractivity of the water could be proved to be present and, moreover, this is a decrease due to cations, an increase due to  $\text{F}^-$ , as the following table shows:<sup>19</sup>

TABLE I.

CHANGE OF THE REFRACTIVITY OF WATER BY DISSOLVED IONS.

$\text{H}^+$ .	$\text{Li}^+$ .	$\text{Na}^+$ .	$\text{Al}^{+++}$ .	$\text{F}^-$ .
- 0.67	- 0.62	- 0.30	- 2.58	+ 0.30

As is evident,  $\text{Na}^+$  exerts a weaker influence than the smaller  $\text{Li}^+$  and the more highly charged  $\text{Al}^{+++}$ . In the case of  $\text{H}^+$ , we probably have to do mainly with the effect of the addition of the hydrogen nucleus to a water molecule, resulting in the formation of the hydroxonium ion  $^{20} \text{H}_3\text{O}^+$  in such a way that this ion, whose radius according to H. G. Grimm<sup>20a</sup> lies somewhere between that of  $\text{K}^+$  and  $\text{Rb}^+$ , like the latter ions produces no definitely demonstrable effect upon the refractivity of the water. In its union with anions the hydrogen nucleus has also a decided consolidating action: thus the value 9.00 of free  $\text{Cl}^-$  sinks to 6.67 in gaseous  $\text{HCl}$ .

<sup>17</sup> In Fig. 1,  $R$  free ions refers to the free gaseous state.

<sup>18</sup> We use the values given by Fajans and Joos. The new measurements change them somewhat.

<sup>19</sup> The values given in the table will in all likelihood suffer certain changes as the result of measurements now in progress.

<sup>20</sup> Cf. *e.g.*, H. Goldschmidt, *Z. physik. Chem.*, 1907, **60**, 728; Fajans, *Naturwiss.*, 1921, **9**, 934; with Joos, *loc. cit.*, p. 31; Hantzsch, *Z. Elektrochem.*, 1923, **29**, 21; Volmer *Ann. Chem.*, 1924, **440**, 200.

<sup>20a</sup> *Z. Elektrochem.*, 1925, **31**, 474.

#### 4. Quantitative Relations.

It is of importance for the following to obtain a quantitative relation between the magnitude of the change of refractivity of anion and the distance between the ions in the lattice. This relation can be best derived from the comparison of the effects in question in the case of LiI and NaI or of LiBr and NaBr, since in these salts the influence of the anion on the cation is very small, so that as a first approximation one may regard the observed effects as due to the action of the cations upon the anions.

If  $\Delta R$  is the diminution in the refractivity of a given anion in the lattice,  $r$  the distance in  $10^{-8}$  cm. between oppositely charged ions, and  $k_A$  a constant, then one finds for the anion in question:

$$\Delta R \times r^4 = k_A.$$

TABLE II.

	$\Delta R.$	$r.$	$k_{I-}.$		$\Delta R.$	$r.$	$k_{Br-}.$
NaI . . .	2.67	3.231	291	NaBr . . .	1.61	2.981	127
LiI . . .	3.46	3.025	290	LiBr . . .	2.31	2.745	131

For the iodides the agreement is perfect. The small deviation of 3 per cent. in the case of the bromides would disappear if we assumed that in the case of NaBr, in which of the four salts the influence of the anion upon the cation is the strongest,  $\Delta R$  is thereby diminished by 0.05. From LiCl one finds for  $k_{Cl-}$  a value of about 70, and the comparison of the three halogen ions shows that  $k_A$  is approximately proportional to the square of the refractivity of the halogen ion. At a later opportunity these relationships will be discussed more in detail.

#### 5. General Remarks on the Experiments.

We have seen that in crystals and in molecules the effect of the ions on one another and in dilute solutions on the surrounding water is to produce plainly evident changes in the refractivity, changes which show simple regularities. It is to be expected that when, upon concentrating an infinitely dilute solution, the ions approaching more closely to each other, thereby displace the water and unite to form undissociated molecules or complex ions, or when they merely "associate," these processes should make themselves perceptible in changes of the refractivity.

Since several effects mutually overlap, we can only expect to arrive at unambiguous conclusions after comparing a fairly large number of salts, taking into account the individual properties of the separate ions, namely their charge, radius, and deformability. The substances hitherto investigated have been chosen from this point of view. They are given in Table V.

Table III. gives the refractivity values of the free gaseous ions in question, which serve as measures of their respective deformabilities. This table needs no explanation except in the two cases of  $ClO_4^-$  and  $SO_4^{--}$ . In spite of their relatively high total refractivity these ions, together with  $F^-$ , are amongst the least deformable anions; this is already partly evident from the results of Niggli<sup>21</sup> and Widman<sup>22</sup> who show that for solid sulphates and analogous salts the refractivity is more nearly

<sup>21</sup> *Z. Kristall.*, 1924, 60, 249.

<sup>22</sup> *Ibid.*, p. 181.

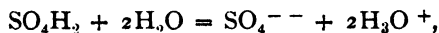
TABLE III.  
 $R_D$  FOR GASEOUS IONS.

$\text{Li}^+$ .	$\text{Na}^+$ .	$\text{K}^+$ .	$\text{H}_3\text{O}^+$ .	$\text{NH}_4^+$ .	$\text{Ba}^{++}$ .	$\text{Al}^{+++}$ .
0.2	0.50	2.23	3.04	4.13	4.28	0.17
$\text{F}^-$ .	$\text{Cl}^-$ .	$\text{Br}^-$ .	$\text{I}^-$ .	$\text{ClO}_4^-$ .	$\text{SO}_4^{--}$ .	$\text{H}_2\text{O}$ (liquid).
2.50	9.00	12.67	19.24	$13.32 \div 4$ = 3.33	$14.63 \div 4$ = 3.66	3.71

additive than it is for the halides; its truth becomes particularly convincing upon examination of numerous other properties of the salts which are related to the deformation of their ions, such as colour, the interionic distance in the crystal lattice, the lattice energy, solubility,<sup>23</sup> and photoelectric conductivity.<sup>24</sup>

The small deformability of these complex anions is easily understood. For it is only those few electron orbits of the anions which are in the immediate neighbourhood of the cation united with it, that will be influenced by the latter; in the comparison of the complex ions in question with the halogen ions for instance, we must, therefore, employ as comparative measures of deformability not the total refractivities of the complex ions, but the respective refractivities per equal number of outer electrons, that is, the refractivities per oxygen octet in each case. Thus we obtain for  $\text{SO}_4^{--}$  the value  $\frac{14.63}{4} = 3.66$ , for  $\text{ClO}_4^-$ ,  $\frac{13.33}{4} = 3.33$ . The former value lies close to that of water.

That the deformability of the sulphate ion actually is very nearly equal to that of water follows convincingly from the fact that the refractivity of sulphuric acid (in concentrations ranging from 30 per cent. up to the nearly pure acid) is, unlike that of HCl and the salts about to be discussed, constant<sup>25</sup> within the limits of experimental error of about 0.02 units of R. Obviously the hydrogen nucleus lowers the refractivity of the  $\text{SO}_4^{--}$  ion to very nearly the same extent as that of the water, so that upon dilution the dissociation taking place according to the equation,



does not make itself evident in an effect upon the refractivity.

## 6. Additivity of the Refractivity at Infinite Dilution.

Having concluded these general remarks, we may now discuss the results expressed in Fig. 2 on the variation of the refractivity of salt solutions with their concentration.

In spite of the numerous earlier measurements of the refractivity of solutions, little of certainty can be said as to the variation of refractivity with concentration. Either the measurements cover an insufficient concentration range or they are, as is shown by the irregularity of the curves, not sufficiently exact. Of the measurements already on hand we could therefore use only

<sup>23</sup> Fajans, *Naturwiss.*, 1923, 11, 165.

<sup>24</sup> Gudden and Pohl, *Z. Physik.*, 1923, 16, 42.

<sup>25</sup> Cheneveau, *Compt. rend.*, 1904, 138, 1483; Dinkhauser, *Wien. Ber.*, 1905, 114, (II A), 1001. Le Blanc and Rohland, *Z. physik. Chem.*, 1896, 19, 261.

those of Hüttig,<sup>26</sup> on LiCl, LiBr, LiI, and HCl. All other results<sup>26a</sup> in Fig.

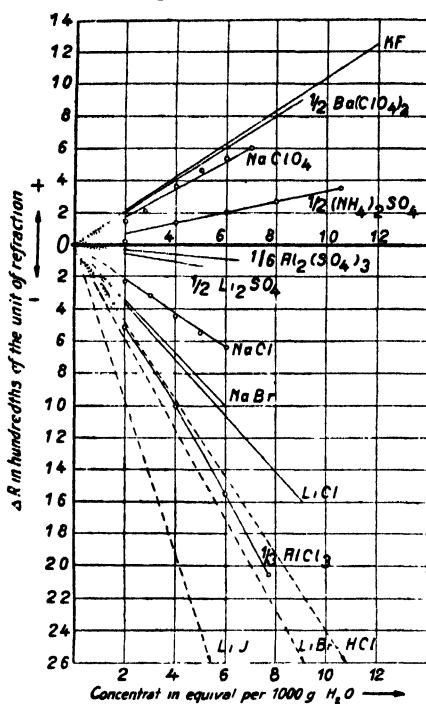


FIG. 2.

refractivity, is shown by the following combination.

TABLE IV.

LiCl . . . . .	8.76	1/2 Li <sub>2</sub> SO <sub>4</sub> . . . . .	8.21
1/3 AlCl <sub>3</sub> . . . . .	7.08	1/6 Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . . . . .	6.57
Difference . . . . .	1.68	Difference . . . . .	1.64

This deviation represents the sum of the experimental errors for four salts. These errors have four sources, as follows:—

1. The influences of traces of impurities possibly present in the salts.
2. Small uncertainties in the analytical determination of the absolute concentration of the salt solutions, particularly difficult in the case of the aluminium salts.
3. The errors in the single values of the refractivity, which for the

<sup>26</sup> Hüttig and Keller, *Z. Elektrochem.*, 1925, 31, 390. Column XI. of Table I. as well as Figs. C and D are somewhat in error due to a mistake in calculation. The as yet unpublished measurements on HCl (Hüttig and Küenthal), I owe to the kindness of Professor Hüttig. Concerning the temperature, cf. note 35A.

<sup>26a</sup> Professor E. Schreiner has kindly informed the author that he has studied the relation of refractivity to concentration in solutions of LiCl and HCl in H<sub>2</sub>O, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH and has found analogous results.

<sup>27</sup> The account of the experiments will be published elsewhere.

<sup>28</sup> Besides the substances given in Table V. BaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> have also been investigated. On account of their low solubilities, the relatively very slight changes with concentration could not be accurately measured. The values for C = 0 are:  $\frac{1}{2}$ Na<sub>2</sub>SO<sub>4</sub>, 7.63;  $\frac{1}{2}$ BaCl<sub>2</sub>, 11.26.

smallest concentration,  $2N$ , have a magnitude of about 0.01 units of refractivity, for concentrations over  $6N$ ,<sup>20</sup> about 0.004 units.

4. The uncertainty involved in extrapolating to  $C = 0$ .

Since of the above four sources of error 1, 2, and 4 exert an influence only upon the absolute value of the refractivity, but not upon its rate of change, the latter contains only the very slight uncertainty to be seen in the points plotted for several of the salts.

## 7. Dependence of Refractivity upon Concentration.

In order that the different variations of refractivity with concentration for the different salts may be readily compared, we have in Fig. 2 plotted as a function of the concentration only the differences between the refractivity at the given concentration and the extrapolated refractivity for  $C = 0$ .

Here we shall disregard those deviations from linearity which in a few cases (KF,  $\text{AlCl}_3$ , HCl) without doubt exceed the limit of experimental error and, for purposes of comparison, arrange (in Table V.) the values of  $R_{5N} - R_{C=0}$  in order in which they grow more positive.

TABLE V.

$R_{C=0}$  AND  $\Delta R = R_{5N} - R_0$  FOR THE D-LINE AT 25°.

	LiI.	LiBr.	$\frac{1}{3}\text{AlCl}_3$ .	HCl.	LiCl.	NaBr.	NaCl.
$R_0$	—	—	8.21	—	8.76	12.90	9.27
$\Delta R$	-0.240	-0.140	-0.130	-0.120	-0.088	-0.083	-0.053
	$\frac{1}{2}\text{Li}_2\text{SO}_4$ .	$\frac{1}{3}\text{Al}_2(\text{SO}_4)_3$ .	$\frac{1}{3}(\text{NH}_4)_2\text{SO}_4$ .	$\text{NaClO}_4$ .	$\frac{1}{3}\text{Ba}(\text{ClO}_4)_2$	KF.	
$R_0$	7.08	6.57	11.70	13.44	15.44	4.86	
$\Delta R$	-0.013	-0.008	+0.015	+0.042	+0.050	+0.055	

If we first examine the behaviour of the halides, as shown in Table V. and in Fig. 2, we find the same regularities as were found to hold in the case of the transition of the ions from the free gaseous state to the crystal, as would be expected from the properties of the ions in question. With increasing concentration there is a decided decrease in refractivity, *i.e.*, a net consolidation, in the case of the salts of the easily deformable anions  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , with the difficultly deformable cations  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ . The effect increases with increasing deformability of the anion ( $\text{LiI} > \text{LiBr} > \text{LiCl}$ ,  $\text{NaBr} > \text{NaCl}$ ), and with increasing field strength of the cation, *i.e.*, either with its decreasing radius ( $\text{LiCl} > \text{NaCl}$ ,  $\text{LiBr} > \text{NaBr}$ ), or with its increasing charge ( $\frac{1}{3}\text{AlCl}_3 > \text{LiCl}$ ).

On the other hand KF, whether upon formation of the crystal from the free ions, or on increase in concentration of its solution, shows an increase in refractivity.

These regularities make it very probable that the observed changes to a large extent at least, are attributable to the fact that in solutions the electronic systems of the ions are influenced by the electric fields of their partners in a manner similar to that shown to be true in the case of their union into crystals and molecules.

## 8. Proof that Direct Contact of the Ions without Intervening Water Molecules Exists.

The question now arises, whether the polarising action of the ions upon each other in the solution can bring about the observed effects, when all

<sup>20</sup> All concentration data are expressed in equivalents per 1000 g.  $\text{H}_2\text{O}$ .

the ions of the electrolyte are separated from each other by water molecules, that is, when the electrolyte is completely dissociated into simple, not complex ions or whether from the character or the magnitude of the effects it is possible to conclude that some of the oppositely charged ions must have approached each other so closely that no water molecules could have been present between them.

Light on this question is obtained on the one hand from a comparison of the respective effects shown by the various ion combinations in solution, on the other hand from contrasting the magnitudes of the effects in solutions with those in crystals. We shall begin with the latter method.

(a) *Quantitative Comparison between the Refractivity in Solutions and in Crystals.*

We compare for LiCl the solution containing 5 moles per 1000 g. H<sub>2</sub>O (density 1.0984) with the crystal.

TABLE VI.

	$\Delta R.$	Vol. per 1 mol. LiCl.	$r_{\text{sol.}}/r_{\text{cryst.}}$	$r.$
5 m. Solution Crystal . . .	$R_{5m} - R_0 = -0.088$ $R_{\text{cryst}} - R_{\text{gas ions}} = -1.61$	220.5 c.c. 20.5 c.c.	2.15	$5.52 \times 10^{-8}$ cm. $2.57 \times 10^{-8}$ cm.

If in the solution the arrangement of all ions were similar to that in the lattice, then the mean interionic distance in the solution and crystal would be proportional to the cube root of the molal volumes, that is, it would be  $r_{\text{sol.}} = 2.15 r_{\text{cryst.}}$ , this gives  $r_{\text{sol.}} = 5.52 \times 10^{-8}$  cm., therefore greater by  $2.95 \times 10^{-8}$  cm. than  $r_{\text{cryst.}}$ . Since the diameter of the sphere of action of one molecule of water is about  $3 \times 10^{-8}$  cm., there would at this mean interionic distance be room for just one molecule of water between the ions.

On the other hand we can calculate what the mean distance  $r_{\text{bm}}$  between the ions in solution, assuming a lattice-like arrangement, would have to be in order that the observed effect 0.088 may be produced, if we use the relation derived in Section 4 ( $\Delta R \cdot r^4 = k$ ), calculating on the basis of the often used assumption<sup>30</sup> that the attractive force between ions, even when very close to each other in aqueous solution, is 80 times smaller than in a vacuum.

$$r_{\text{bm}} = \sqrt[4]{\frac{1.61}{0.088 \times 80}} \times 2.57 \times 10^{-8} = 0.69 \times 2.57 \times 10^{-8} \text{ cm.}$$

We thus arrive at the quite absurd conclusion that the mean interionic distance is not 2.15 times greater than  $2.57 \times 10^{-8}$  cm. but only 0.69 times greater; this means that the mean interionic distance would have to be smaller in the solution than in the crystal lattice.

The reason of this absurd result can be found firstly in the fact that the value of 80, used for the dielectric constant, is almost certainly too large in the immediate neighbourhood of the ions. On the other hand, in order to explain the observed optical effect on the assumption of a lattice-like arrangement of the ions in the solution under consideration, we should have to ascribe to the dielectric constant the value

$$80 \times \left( \frac{0.69}{2.15} \right)^4 \approx 1$$

which again is impossibly small for this solution as a whole.

<sup>30</sup> Cf. e.g. Bjerrum, *Danske Videnskab. Selskab.*, 1926, VII., 9.

From this it follows, that the observed effect must be produced by the fact that a certain proportion of the ions approach within a distance from each other which is distinctly less than the actual mean distance,  $5.52 \times 10^{-8}$  cm.<sup>31</sup> Since, when the ions are separated even by this mean distance, there is room but for one water molecule between them, these approaches must involve direct contact of the two ions. Any rigorous quantitative conclusions however are impossible, since it is not exactly known what ratios the magnitudes of the consolidating effects in the lattice bear to those in the molecule, in the complex ion or in an "associated" ion pair. We will only mention that if we wish to attribute the observed effect to the formation of associated ion pairs and assume that the change accompanying the formation of a mole of such pairs is equal to that accompanying the formation of a mole of crystals, we have to distinguish between the two following limiting cases. If *all* the ions were joined in pairs, which is certainly not the case, since the conductivity of the concentrated solution is still one-third of that at infinite dilution, we should have to give *D* the value 18. If, however, we consider the observed effects as the result of a contact between the ions so intimate that we can neglect the influence of the surrounding medium and make *D* = 1, then we should arrive at a degree of association of 5.5 per cent, which would naturally be much nearer the truth than a value of 100 per cent.

(b) *Comparison of the Effects for Different Electrolytes.*

This comparison leads to the same affirmative conclusion as to the existence in appreciable quantities of undissociated ion combinations in solution.

We obtain particularly valuable insight from the as yet undiscussed behaviour of HCl. If we compare the relative magnitudes of the observed consolidating effects, we find for solutions of equal concentration:

$$\text{NaCl} : \text{LiCl} : \text{HCl} = 1 : 1.7 : 2.3.$$

At all events it is to be expected that the  $\text{Cl}^-$  ions, subject to the action of univalent cations, will suffer a decrease in refractivity which is greater, the more closely the centres of the cation can approach a  $\text{Cl}^-$  ion, and the greater the number of  $\text{Cl}^-$  ions which possess one or more cations within a definite sphere of consolidating action.

If we adopt strictly the point of view of the electrostatic theory (*i.e.*, if we disregard the individual characteristics<sup>32</sup> of the various ion combinations present), the number of particles influenced in the way just mentioned is the greater, the more closely the ions can approach each other. Upon this basis we can thus unambiguously conclude from the greater decrease in refractivity for LiCl than for NaCl that, in the solution as in the crystal, the  $\text{Li}^+$  ions can approach more closely to the  $\text{Cl}^-$  ions than can the  $\text{Na}^+$  ions. This conclusion is valid whether the ions, even in their closest approaches to each other, remain hydrated (*i.e.*, separated by water molecules), or whether they can come into direct contact with each other. Hence, since the parameter introduced by Debye and Huckel has a greater value for LiCl than for NaCl, it can hardly have the physical significance ascribed to it, namely that of the smallest possible distance between the ions in the solution.

<sup>31</sup> According to Reis (*Z. Physik.*, 1, 294, 1920), as well as to Born and Heisenberg, *ibid.*, 1924, 23, 388, the interionic distance in the gaseous molecules of the alkali halides is about 20 per cent. smaller than in the corresponding lattices.

<sup>32</sup> As regards such individual characteristics *cf.* particularly "The Theory of the Interaction of Ions" by Brönsted, *J. Am. Chem. Soc.*, 1922, 44, 877, and Güntelberg, *Z. physik. Chem.*, 1926, 123, 199.

In the case of hydrochloric acid we must take into consideration the following possible conditions in the solution:—<sup>33</sup>

1. Undissociated molecules,  $HCl_{und}$ .
2. By taking up a molecule of water,  $HCl$  dissociates forming  $H_3O^+$  and  $Cl^-$ . The ions of the salt  $H_3O^+ \cdot Cl^-$  which is known also in the solid state<sup>34</sup> can remain very close to each other in the solution, in the state of undissociated molecules or "associated" ion pairs.
3. By the interposition of one or several further molecules of water, a dissociation into hydrated ions  $H_3O^+$  and  $Cl^-$  takes place.

If now the solution contained only conditions 2 and 3 in appreciable quantities, then the  $H_3O^+$  ion alone could have a consolidating effect upon the  $Cl^-$  ions. Now the  $H_3O^+$  ion lies close to  $NH_4^+$  and  $Rb^+$  as regards magnitude and deformability and, furthermore, for  $RbCl$  no effect could be found even in the case of the formation of crystal from free ions. Therefore  $H_3OCl$  also would show no change or in any case a change much less than that for  $NaCl$ . In reality, however, the rate of change for  $HCl$  is 2.3 times as great as that for  $NaCl$ .

These relationships, however, can be explained without difficulty, if one assumes that in  $HCl$  solutions a certain proportion of the  $H$  nuclei unites directly with the  $Cl^-$  ions, for we know that upon the formation of gaseous  $HCl$ , the refractivity of the  $Cl^-$  ion decreases greatly (from 9.00 to 6.67), and what is more, after what has been said above, practically the whole effect in the solution would have to be due to this union of the  $H$  nuclei with the  $Cl^-$  ions. As a matter of fact the existence of undissociated  $HCl$  in aqueous solution follows from the measurable partial pressure of  $HCl$  in not too dilute solutions. For quantitative information cf. section 9.

The union of ions with accompanying displacement of the water surrounding them, in the case of  $HCl$ , is not to be considered due only to the circumstances that the  $H$  nucleus is able to penetrate into the electron shells of the  $Cl^-$  ion and that the  $HCl$  molecule, as generally assumed today, has a structure more closely allied to that of non-polar compounds than to that of the typical salts; for the behaviour of  $NaClO_4$  also, which, in Fig. 2, shows a great increase of refractivity, can only be understood by assuming intimate contact of the two ions without the presence of intervening water.

The behaviour of  $Ba(ClO_4)_2$ , which likewise shows a strongly positive change is only understood, if one recalls the fact (section 2) that under similar conditions of radius and deformability, anions act more strongly on cations than cations on anions—a fact which makes itself evident in the behaviour of  $KF$  also in solution. The polarisability of  $Ba^{++}$  distinctly exceeds that of  $\frac{1}{2} ClO_4^-$ . But we must remember that  $Ba^{++}$  is doubly charged and is certainly smaller than the singly charged  $ClO_4^-$ . On the other hand the positive change for  $(NH_4)_2SO_4$  is on this basis easily understood, since here the anion, although having a greater radius, is less deformable and more highly charged than the cation.

In order to understand the behaviour of  $NaClO_4$ , we must compare the changes of refractivity for  $NaF$ ,  $(NH_4)_2SO_4$  and  $NaClO_4$ .

$NaF$ , which is too insoluble to be investigated directly by the present methods would in all probability show no rate of change, since here also there is no difference between the solid salt and its infinitely dilute solution,

<sup>33</sup> Cf. e.g. Hantzsch, *Ber.*, 1925, 58, 612.

<sup>34</sup> Cf. Abegg, *Handbuch anorg. Chem.*, 1913, IV, 137; Grimm, *Z. Elektroch.*, 1925, 31, 474.

whereas the magnitude of the positive rates of change for  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaClO}_4$  bear the following ratios to one another :

$$\frac{1}{2}(\text{NH}_4)_2\text{SO}_4 : \text{NaClO}_4 = 1 : 2.8.$$

Were we to assume that in these three salts all the ions are separated from each other by layers of water, we could not explain why  $\text{NaClO}_4$  should have a positive rate of change almost as great as that of  $\text{KF}$ , while  $\text{NaF}$  shows no rate of change: for an extensive loosening of the very slightly deformable  $\text{Na}^+$  ion ( $R = 0.5$ ) is scarcely to be expected and, should this loosening nevertheless be possible, it would be caused more readily by the field of the  $\text{F}^-$  ion than by that of the  $\text{ClO}_4^-$  ion, since the former is smaller and hardly more deformable than the latter. Finally it would be altogether incomprehensible why the positive rate of change for  $\text{NaClO}_4$  is even greater than that for  $(\text{NH}_4)_2\text{SO}_4$ , since on the one hand  $\text{NH}_4^+$  is much more deformable than  $\text{Na}^+$ , and on the other hand  $\text{SO}_4^{--}$ , because of its double charge must act more strongly upon the cations than does  $\text{ClO}_4^-$ . To attribute the lower position of the  $(\text{NH}_4)_2\text{SO}_4$  curve only to the somewhat greater deformability of the  $\text{SO}_4^{--}$  ion is impracticable, for in that case the sulphates of the  $\text{Li}^+$ , and  $\text{Al}^{+++}$  ions, which possess a much greater deforming power than  $\text{NH}_4^+$ , would have to show strongly negative rates of change.

All these contradictions however disappear, if we make the assumption that here also, as in the case of  $\text{HCl}$ , the rates of change arise solely from a direct union of the water-free (desolvated) ions with each other. We have seen (Section 3) that  $\text{Na}^+$  lowers the refractivity of the water surrounding it by altogether 0.3 units; if the water is pushed away and its place is taken by an anion such as  $\text{ClO}_4^-$  which is less deformable than water, the introduction of a positive component into the change of the refractivity results, to which there is further added the effect of the loosening of the  $\text{Na}^+$  ion by the anion. Superimposed upon this is an effect of opposite sign, whenever the free anion exerts a loosening influence upon the water which is subsequently obliterated by the anion's union with the cation. Since now the small  $\text{F}^-$  ion loosens the water molecules more extensively (*cf.* Table I.) than the  $\text{ClO}_4^-$  ion, it is not surprising that the rate of change for  $\text{NaClO}_4$  is more positive than for  $\text{NaF}$ . The approximately equal deformabilities of  $\text{SO}_4^{--}$  and  $\text{H}_2\text{O}$  explain further, why for the sulphates even of such powerfully deforming ions as  $\text{Li}^+$  and  $\text{Al}^{+++}$  only a very slight effect is to be observed: the substitution of water by  $\text{SO}_4^{--}$  causes no considerable change; the very small deformability of these cations, however, unlike  $\text{NH}_4^+$ , allows no positive effect to be produced.

### 9. Undissociated Molecules ( $\text{HCl}_{und.}$ ) and the Complex ion $\text{H}_2\text{Cl}^+$ in Hydrochloric Acid Solutions.

All the facts and relationships cited thus agree in leading to the conclusion that in concentrated solutions of the most varied kinds of strong electrolytes, a part of the ions come together without being separated by intervening water molecules and, what is more, the contact between them must be very intimate, since the dielectric constant of the medium seems (section 8 a) to exert no influence, or at most a slight one upon the magnitude of the observed optical effects. And now the question arises, whether these intimate approaches of the ions to each other involve the formation of neutral undissociated molecules or that of complex ions, or, to put it more exactly, what fractions of the total quantity of the electrolyte is present in the one or the other state.

The approximate linearity of the changes obtained would be very simply explained by attributing the change in each case to the union of *two* ions to form a molecule (in the case of electrolytes with ions of equal valence) or to form a complex ion (in the case of electrolytes containing ions of different valence). For, in the case of strongly dissociated binary electrolytes the undissociated fraction, according to the Ostwald dilution law, is simply proportional to the concentration. But beyond the fact that at the high concentrations in question the quantitative relations are rendered complex by the necessity for taking into account the activity coefficients of the ions, a closer examination of hydrochloric acid shows that the state of affairs cannot be so simple.

Several years ago, on the assumption that the diminution of refractivity of HBr with increasing concentration is due to the formation of undissociated molecules HBr, I roughly estimated<sup>35</sup> on the basis of the measurement of A. Heydweiller their proportion to be about 3 per cent. of the total HBr in a 4*N* solution. In the same way E. Schreiner<sup>35</sup> found 5.4 per cent. for a 4*N* solution of HCl.

If the conditions  $HCl_{und.}$ ,  $H_3O \cdot Cl$  and the hydrated ions  $H_3O^+$  and  $Cl^-$  were the only ones possible in the HCl solution, we should to-day be able to put such a calculation of the proportion of undissociated HCl upon a much sounder basis, for we have been able by the above comparison with other chlorides to show that practically the entire change really is attributable to the union of the H nuclei with the  $Cl^-$  ions. We then have the measurements of Hüttig<sup>36a</sup> and Kukenthal, which are more accurate than the preceding ones.

TABLE VII.  
REFRACTIVITY OF HCl SOLUTIONS AT 20°.

$$\begin{array}{cccc} m & 0 & 5 & 16 \\ R_m & 8.58 & 8.46 & 8.25 \end{array} \quad \text{and } R_{\text{gas}} = 6.67$$

whence:  $R_0 - R_{\text{gas}} = 1.91 \quad R_0 - R_{5m} = 0.120.$

Hence for a 5*m.* solution the undissociated fraction is

$$1 - \alpha = \frac{0.120}{1.91} = 6.3 \text{ per cent.}$$

Linear extrapolation from this value up to  $\alpha = 1$  for  $c = 0$  yields for a concentration of 0.01 *m.* the value of  $1 - \alpha = 0.00012$ , corresponding to a concentration of undissociated HCl of  $1.2 \times 10^{-6}$  *m.*

Now Ebert<sup>26</sup> has attempted to estimate the concentration of undissociated HCl in a 0.01 *m.* solution from its calculable vapour pressure of  $2.86 \times 10^{-8}$  *mm.* at 25° on the assumption that the distribution ratio, solution/gas for undissociated HCl can be deduced from those of the alkyl chlorides. He obtains as a lower limit for the concentration of undissociated HCl in the 0.01 *m.* solution a value of  $5.9 \times 10^{-12}$  *m.*, which is  $2 \times 10^5$  times smaller than that calculated above.

This estimation of Ebert is based upon a valuable idea. It is, however, better to compare HCl with HCN rather than with the alkyl chlorides. The solubility of a gas in water is very probably largely determined, like its condensability, by its electric moment and by the polaris-

<sup>35</sup> In a lecture held in Christiania in 1923, communicated by E. Schreiner, *Naturwiss.*, 1925, 13, 245.

<sup>36a</sup> Hüttig's measurements were made at 20°, but for LiCl they show within the limits of experimental error the same rate of change as our experiments at 25°.

<sup>36</sup> *Naturwiss.*, 1925, 13, 393.

ability of its electron shells. The latter factor, as measured by the refractivity, is very nearly equal for HCl (6.67) and HCN (6.47). The dipole moment of HCN is, however, very probably somewhat greater than that of HCl, since both the boiling-point and the molal polarisation,<sup>37</sup>

$$P = \frac{D-1}{D+2} \cdot \frac{M}{d} \text{ where } D \text{ is the dielectric constant,}$$

are higher for HCN than for HCl.

TABLE VIII.

	B.P.	Molal Polarisation P.
HCl	- 85.0°	25.5 at 27.7°
HCN	+ 25.6° <sup>38</sup>	38.5 <sup>39</sup> „ 22°

One would therefore expect HCN to have a greater distribution ratio, solution/gas than HCl. Measurements<sup>40</sup> of the partial vapour pressure of the almost completely undissociated HCN from its solutions in water, give the following values :

TABLE IX.

PARTIAL VAPOUR PRESSURE OF HCN IN AQUEOUS SOLUTION AT 18°. <sup>40</sup>

Mols. of undiss. HCN per 1000 g. H <sub>2</sub> O	9.79	6.17	2.92	1.9	4 × 10 <sup>-10</sup>
Partial pressure in mm.	349.5	283.4	167.0	121	2.86 × 10 <sup>-8</sup>

The last two values are obtained by extrapolation<sup>41</sup> of the other three. After what has been said it is clear that we may probably regard the value  $4 \times 10^{-10}$  m. as an upper limit of the concentration of *HCl*<sub>und.</sub> at 18° corresponding to the partial pressure  $2.86 \cdot 10^{-8}$  mm.

In order to obtain values for 25° we need to use the theoretical heat of solution of HCl gas to form undissociated HCl. We can roughly estimate it by taking the average value of the heats of vaporisation of liquid HCl (3.6 Cal.) and H<sub>2</sub>O (10 Cal.) respectively, that is 7 Cal.

This gives for 25°: 0.01 m. HCl;  $p = 2.86 \times 10^{-8}$  mm.; upper limit for undiss. HCl =  $3 \times 10^{-10}$  m.<sup>42</sup> This upper limit is considerably higher than the lower limit  $5.9 \times 10^{-12}$  m. estimated by Ebert, but it is nevertheless 4000 times smaller than the value  $1.2 \times 10^{-6}$  m. obtained from the refractivities, on the basis of the assumption that  $\Delta R$  of the 5m. solution is due only to undissociated HCl.

This contradiction could be removed by the assumption that the union of the H nuclei with the Cl<sup>-</sup> ions results in the formation not only of *HCl*<sub>und.</sub>,

<sup>37</sup> Ebert, *Z. physik. Chem.*, 1924, 113, 1; Debye in Marx, *Handb. d. Radiol.*, 1925, 6, 603.

<sup>38</sup> Bredig and Teichmann, *Z. Elektrochem.*, 1925, 31, 449.

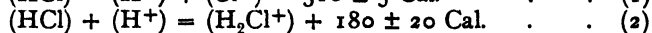
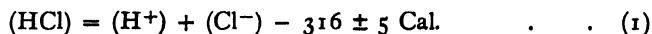
<sup>39</sup> Ebert, *ibid.*, p. 454.

<sup>40</sup> Bredig and Shirado (as yet unpublished). I am indebted to the authors for permission to use these figures.

<sup>41</sup> In these and the following calculations I was kindly assisted by Mr. O. Koenig.

<sup>42</sup> From this upper limit, using the value of 0.92 for the activity coefficient of the ions in the 0.01 N solution we calculate the lower limit for the dissociation constant of HCl to be  $2.7 \times 10^5$ . The true value is probably closer to this lower limit than to the upper one estimated by Ebert to be  $10^7$ . Schreiner (*Naturwiss.*, 1925, 13, 245; *Z. Physik. Chem.*, 1924, 111, 419) who made the first calculations of the dissociation constant of HCl, arrived at values lying between  $10^{2.3}$  and  $10^6$ .

but also of the complex cation  $\text{H}_2\text{Cl}^+$ .<sup>43</sup> In fact thermochemical considerations make it probable that the formation of  $\text{H}_2\text{Cl}^+$  from undissociated molecules is, in solution, possible of its own accord. For the gaseous state we have, on the one hand equation (1), on the other hand according to calculations by Hund,<sup>44</sup> based on atomic models, equation (2):



From this there follows for the gaseous state:



In the gaseous state the system  $\text{H}_2\text{Cl}^+ + \text{Cl}^-$  is thus strongly endothermic, that is unstable with respect to  $2\text{HCl}$ . But if we consider the process in aqueous solution, this negative quantity is increased by the heat of solution of  $2\text{HCl}$  to  $2\text{HCl}_{\text{und.}}$ , that is by about 14 Cal. giving  $-150 \pm 25$ , on the other hand however we gain the large heat of solution of the gaseous ions (their heats of hydration).<sup>45</sup> For dilute solutions that of  $\text{Cl}^-$  is about 80 Cal.; if one sets that of  $\text{H}_2\text{Cl}^+$  about equal to that of  $\text{Cs}^+$ , which has a value of about 70 Cal., one thus obtains from the hydration process 150 Cal. which might compensate the above  $-150 \pm 25$  Cal. At very high concentrations, however, the equilibrium of the reaction,



on account of the greatly lowered relative water content must be shifted so as to result in an increase of the  $\text{HCl}_{\text{und.}}$  concentration at the expense of  $\text{H}_2\text{Cl}^+$ .

These relationships probably form one of the reasons why it is only for small concentrations that the partial pressure of  $\text{HCl}$  increases, according to the law of mass action and to the distribution law, approximately proportionally to the square of the total concentration, whereas at high concentrations, the increase is much more rapid, as the following figures show:—

TABLE X.<sup>47</sup>

PARTIAL VAPOUR PRESSURE OF  $\text{HCl}$  FOR SOLUTIONS OF HYDROCHLORIC ACID AT  $25^\circ$ .

m	0.001	0.01	0.1	1	5	10	16
p	$3.24 \times 10^{-10}$	$2.86 \times 10^{-8}$	$2.22 \times 10^{-6}$	$2.27 \times 10^{-4}$	$5.30 \times 10^{-2}$	4.20	160 mm.

Examining the behaviour of 16 m.  $\text{HCl}$  we find at  $25^\circ$  a partial pressure of 160 mm. From the heat of solution of  $\text{HCl}$  to  $\text{HCl}_{\text{und.}}$ , estimated above to be 7 Cal., we calculate the partial pressure at  $18^\circ$  of the solution containing the same proportion of undissociated  $\text{HCl}$  to be 121 mm. For  $\text{HCN}$  this pressure, according to the measurements of Bredig and Shirado at  $18^\circ$  corresponds to a concentration of about 1.9 m. This would therefore

<sup>43</sup> The cation  $\text{H}_2\text{F}^+$  as analogous to  $\text{H}_2\text{N}^+$  and  $\text{H}_2\text{O}^+$  is mentioned by Grimm (*Chemiker Kalender*, 1925, p. 63, Fig. 16). Cf. also, Drucker and Riethof, *Z. physik Chem.*, 1924, III, 32. Bronsted, *J. physical Chem.*, 1926, 30, 777.

<sup>44</sup> *Z. Physik.*, 1925, 32, 18.

<sup>45</sup> Fajans, *Naturwiss.*, 1921, 9, 729.

<sup>46</sup> The refractivity of  $\text{H}_2\text{Cl}^+$  is probably about 5, since the consolidation upon formation of  $\text{H}_2\text{Cl}^+$  from  $\text{HCl}$  must be smaller than that upon formation of  $\text{HCl}$  (6.67) from  $\text{Cl}^-$  (9.00). The refractivity of  $\text{Cs}^+$  is 6.2, that is nearly equal to that of  $\text{H}_2\text{Cl}^+$ ; consequently also the radius and the heat of hydration of  $\text{Cs}^+$  and  $\text{H}_2\text{Cl}^+$  are nearly equal.

<sup>47</sup> Of these figures the two next to the last are the result of direct measurements of S. J. Bates and H. D. Kirchman (*J. Am. Chem. Soc.*, 1919, 41, 1991), the others being calculated from them and from the activity coefficients of G. A. Linhart (*ibid.*, p. 1175).

be the upper limit for the concentration of  $HCl_{und.}$  in the 16 m. solution at 25°. This estimate is a high one, since at these great concentrations there is present in HCl solutions a salting-out effect<sup>48</sup> of the ions upon the undissociated molecules, which is absent in the case of HCN.

On the other hand, on the assumption that in the 16 m. solution there is present besides the ions  $H_3O^+$  and  $Cl^-$  practically nothing but undissociated HCl, *i.e.*, practically no  $H_2Cl^+$  ions, we find from the measurements of Hütig ( $R = 8.25$  for 16 m.) the undissociated proportion to be  $(8.58 - 8.25) : 1.91 = 17.3$  per cent., which corresponds to a concentration of undissociated HCl of  $0.173 \times 16 = 2.8$  m., a value which though still distinctly higher than the above calculated upper limit 1.9 m., is nevertheless of the same order of magnitude. These very rough calculations cannot possibly justify any quantitative conclusions as to the actual proportion of  $HCl_{und.}$  and of  $H_2Cl^+$  in this very concentrated solution; but at all events they lend strong support to the view that, with increasing concentration, equilibrium (4) is strongly shifted in favour of the undissociated HCl.

In 5 m. HCl in which, judging from the partial pressure, the concentration of  $HCl_{und.}$  would have to be less than  $7 \times 10^{-4}$  m., we calculate (assuming that practically the whole optical effect is due to formation of  $H_2Cl^+$ ) the proportion of the  $H_2Cl^+$  ion to the total HCl to be 4.4 per cent. corresponding to a concentration of 0.22 m.  $H_2Cl^+$  as follows:<sup>49</sup>  $\Delta R$  for this solution is  $-0.120$ , and if we ascribe to the  $H_2Cl^+$  ion a refractivity 5.0 and also take into account that upon its formation one  $Cl^-$  ion disappears ( $-9.00$ ), while simultaneously  $2H_2O$  are formed from  $2H_3O^+$  ( $+2 \times 0.67$ ) we have

$$\frac{-0.120}{-9.00 + 5.0 + 1.3} = 4.4 \text{ per cent.}$$

Other methods must be used to prove whether this relatively very high value is real. (See p. 375.)

### 10. Incomplete Dissociation of Salts into Simple Ions.

In seeking an explanation of the refractometric effects for salts, we are also led to imagine them as due to formation of molecules and complex ions. For on the one hand the effects for salts are of the same order of magnitude as for HCl; on the other hand it seems to follow from the calculation in section 8*a*, that these effects must be due to a very intimate contact of the ions, since the dielectric constant of the environment has little or no influence upon the forces causing the effects. The following facts lend support to the same idea of an incomplete dissociation of the salts into atom ions.

A few years ago<sup>50</sup> the author called attention to the peculiar gradation in solubility presented by the alkali halides. Here only the values for the chlorides will be cited.

The solubility shows a decided minimum for KCl. This means that at 0° under the action of the hydrating forces,  $K^+$  and  $Cl^-$  have the smallest

<sup>48</sup> Cf. for instance Manchot, *Z. anorg. Chem.*, 1924, 141, 45.

<sup>49</sup> On the basis of the above assumption it is to be expected that in dilute solutions the fraction of the total HCl present as  $H_2Cl^+$ , and therefore also the decrease in the refractivity, would vary as the square of the concentration. In solutions of concentration greater than 1 m., such as have been hitherto investigated, the quantitative relationships are inextricably complex and therefore the linearity in Fig. 2 is not easy to explain.

<sup>50</sup> Fajans, *Naturwiss.*, 1921, 9, 729.

TABLE XI.

SOLUBILITY AT 0° IN MOL. PER 1000 g. H<sub>2</sub>O AND VAPOUR PRESSURE IN mm.  
OF SOLUTIONS 2 m. AND 6 m. AT 100°.

	LiCl.	NaCl.	KCl.	RbCl.	CsCl.
Solubility . .	27.1	6.1	3.85	6.37	9.85
for 2 m. . .	702.5	709	712	710	707.5
for 6 m. . .	541	585	603	600	—

tendency to separate from each other out of their union in the crystal into the state of free dissolved ions.

We then together with Holstamm<sup>51</sup> called attention to the fact that analogous regularities are shown by the vapour pressures of solutions of the alkali halides of equal concentration at 100°. The figures of Table XI.<sup>52</sup> show for KCl for the 2 m. solution and for the 6 m. solution a maximum of vapour pressure, that is a minimum of the lowering of vapour pressure and a minimum of the osmotic coefficient. Since in dilute solutions the osmotic coefficient is known to decrease regularly from Li<sup>+</sup> to Cs<sup>+</sup>, we must probably explain this minimum on the assumption that among the concentrated solutions of the alkali chlorides those of KCl contain fewer ions than the others.<sup>53</sup> In solution the undissociated molecules or complex ions thus pass into the state of atom-ions at 100° with the greatest difficulty in the case of KCl—a result corresponding to that obtained for the crystal state at 0°.

## II. Summary.

### 1. The relationship

$$\Delta R \cdot r^4 = k$$

holds between the decrease in refractivity  $\Delta R$  suffered by a halogen ion in the alkali halide lattice, and the lattice distance  $r$ . The constant  $k$  for the ions I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup> is approximately proportional to the square of their respective refractivities.

2. On the basis of the measurements of Huttig, Keller, and Kükenthal, as well as those of Fajans, Kohner, and Geffken, it is shown that the refractivity of salts and of HCl suffer changes with increasing concentration, which are altogether analogous to the changes which, according to Fajans and Joos, accompany the union of the ions in question into crystals or molecules. These changes are in all cases attributed to the polarising action of the ions upon each other.

3. From the character and the magnitude of these changes it is concluded that in solutions they must be caused by such oppositely charged ions as are separated from each other by approximately the same distance as in the crystal, *i.e.*, by such ions as are in direct contact with each other, with no water molecules between them.

4. From the refractivity data it follows that in solution the least distance to which a Cl<sup>-</sup> ion can approach a cation is greater for Na<sup>+</sup> than for Li<sup>+</sup>.

<sup>51</sup> *Naturwiss.*, 1923, 11, 165; Holstamm, *Diss. München*, 1925.

<sup>52</sup> Interpolated from the measurements of Tammann, *Mem. Acad. Petersbourg* (7), 1887, 35. Landolt-Börnstein, *Physikalisch-chemische Tabellen*.

<sup>53</sup> This consideration is similar to that employed by Harned (*Z. physik. Chem.*, 1925, 117, 49) as well as by Bjerrum (*Erg. exakt. Naturwiss.*, 1926, 5, 140), who from the fact that the gradation of the activity coefficients of NaOH and KOH runs oppositely to that of the Na and K salts, concluded that NaOH is incompletely dissociated in solution.

Since the characteristic parameter introduced into the theory of Debye and Hückel has a greater value for  $\text{Li}^+$  than for  $\text{Na}^+$  this parameter can hardly have the physical significance ascribed to it by the theory, namely that of the distance of nearest approach of the ions.

5. From the comparison of the partial vapour pressures of  $\text{HCl}$  and  $\text{HCN}$  over their aqueous solutions, the latter as given by the measurements of Bredig and Shirado—it is concluded that, up to concentrations of about 5 moles  $\text{HCl}$  per 1000 g.  $\text{H}_2\text{O}$ , the decrease in the refractivity of the  $\text{HCl}$  with increasing concentration of its solution is due only to a very slight extent to the formation of undissociated  $\text{HCl}$ , possibly being caused by the complex ion  $\text{H}_2\text{Cl}^+$ . For still higher concentrations the equilibrium is strongly shifted in favour of the undissociated  $\text{HCl}$ .

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### GENERAL DISCUSSION.

**Professor Brönsted** expressed doubt as to the justification for some of the quantitative conclusions from refractometric data; for instance regarding the suggested formation of  $\text{H}_2\text{Cl}^+$  ions as an explanation of the refractivity in strong  $\text{HCl}$  solutions. The acid dissociation constant of  $\text{HCl}$  was more than  $10^{20}$  times that of  $\text{H}_2\text{O}$  when both substances are present in water solution. Since the conductivity of  $\text{HCl}$  in the pure liquid state was of the same order of magnitude as that of pure water, it could be concluded—disregarding the effect of the dielectric constant—that the basicity of  $\text{HCl}$  was about  $10^{20}$  times less than that of  $\text{H}_2\text{O}$ . Even if there were a considerable effect of the dielectric constant in the opposite direction it seemed, from this calculation, impossible to imagine refractometrically detectable amounts of  $\text{H}_2\text{Cl}^+$ .<sup>1</sup>

For the assumption of a displacement of  $\text{H}_2\text{O}$  molecules in cation-hydrates on close approach of anions, it would be of value to examine the behaviour of the stable metalamines in which such a displacement was not likely to occur.

**Professor Fajans** replied that Professor Brönsted had indicated in the paper just cited, that one could conclude from the equality of the order of magnitude of the specific conductivities of pure  $\text{HCl}$  and  $\text{H}_2\text{O}$ , that the concentration of  $\text{H}_2\text{Cl}^+$  in liquid  $\text{HCl}$  was approximately equal to that of  $\text{H}_3\text{O}^+$  in water. Furthermore, it could be said with certainty that the equilibrium  $2\text{HCl} \rightleftharpoons \text{H}_2\text{Cl}^+ + \text{Cl}^-$  must lie much more to the right in water than in pure  $\text{HCl}$ , because of the higher dielectric constant of water, or more correctly, because the energy of solvation of the ions in water must be larger than in  $\text{HCl}$ . Therefore  $\text{H}_2\text{Cl}^+$  must be present in aqueous hydrochloric acid in finite concentration. There was wanting, however, a sure foundation for a quantitative estimation of the amount. One could, indeed, conclude with Professor Brönsted from the conductivity data, that the product of the acidic and basic dissociation constants of  $\text{HCl}$  in  $\text{HCl}$  was approximately equal to the corresponding product for  $\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ . It did not follow from that, however, that when the acidic constant of  $\text{HCl}$  in  $\text{H}_2\text{O}$  was  $10^{20}$  times greater than the acidic constant of  $\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ , the ratio of the basic constants in  $\text{H}_2\text{O}$  must be inverse. It must be

<sup>1</sup> See Brönsted, *Ÿ. physical Chem.*, 30, 777 (1926).

admitted, nevertheless, that the basic properties of HCl could only be very weak and that therefore one obtained improbably high concentrations of  $\text{H}_2\text{Cl}^+$  on the assumption that the refractometric effects in solutions of HCl under 5 molar were chiefly due to the formation of that ion. It was possibly not right to conclude, from a comparison with the case of RbCl that  $\text{H}_3\text{OCl}$  should not cause a dependence of refraction on the concentration. An investigation of other acids and of ammonium salts would probably settle the question.

**Professor G. Hevesy** remarked that a well-established case of the presence of complex monovalent ions was found in silver nitrate solutions. The "half-valent" silver ions, the presence of which was ascertained by Kohlrausch, Richards, and others, in silver nitrate solutions in the presence of silver, were complex monovalent silver ions.

**Professor Bjerrum** said that so far as he understood, the changes of refraction of strong electrolytes were but small, even in concentrated solutions only of the order of magnitude 1 per cent. He pointed out that the smallness of these changes constituted important support for the hypothesis of complete ionisation of strong electrolytes. The small changes of refraction found by Professor Fajáns seemed, apart from such special cases as HCl, to be explainable by means of the deforming action exerted on each other by oppositely charged ions. Thus even these small changes need not be interpreted as showing the existence of small amounts of unionised molecules in concentrated solutions.

**Professor Fajáns** said that Professor Bjerrum was quite right in regarding<sup>2</sup> the want of a readily apparent dependance of the optical properties of strong electrolytes on the concentration, as an important support of the conception that strong electrolytes were dissociated to a much greater degree than had been assumed by Arrhenius. Since that conception had nullified the older methods of determining the possible undissociated fraction, it was only natural that the assumption of practically complete dissociation was made. Proof of this assumption, obtained till now from the theory of Debye and Hückel (outside the problematic ionic radius) by means of osmotic data, activity coefficients and conductivities, showed that for a number of univalent electrolytes below a concentration of 0.01M the undissociated part, which on the older theory had been assumed to be about 6 per cent. at that concentration, was not perceptible, *i.e.* it was under 1 or 0.5 per cent. It had now been shown that the light absorption (*cf.* the papers of Halban, Ebert, Scheibe, Hantzsch, referred to in footnote 3 of p. 357), as well as the refraction of strong electrolytes depended on the concentration. Doubt was therefore thrown on the accuracy of the assumption of practically complete dissociation at all concentrations.

The optical properties also made it possible to draw more far-reaching quantitative conclusions than were obtainable by means of the other methods mentioned. For, on the assumption that the effects of Fig. 2 were in every case to be traced to the formation of undissociated molecules the amount of these in a 5M solution was found to be, as a rough estimate, a few per cent., for a concentration of 0.01M of the order of  $\frac{1}{100}$  per cent. The numbers were small, but could not, if they were real, be looked on as supporting *complete* dissociation; especially since for HCl, for which there was complete agreement as regards the existence of undissociated molecules in the solution, the concentration of  $\text{HCl}_{\text{undiss.}}$  obtained from its partial pressure was still smaller.

<sup>2</sup> *Z. anorg. Chem.*, 1909, 63, 146.

If solutions of NaOH (in which one ion could not as in HCl penetrate into the electron shell of the other) contain undissociated molecules,<sup>3</sup> this should be possible for NaCl also. By a molecule of NaCl he (Professor Fajans) understood that state of union of the ions which was present in NaCl vapour, and the molecules thus defined must also be present, hydrated of course by orientated water molecules, in the solution in a finite amount owing to the distribution law. One would naturally look on a NaCl molecule as consisting of ions, and the main difference between strong and weak electrolytes was, that the ions in the molecules of the former were weakly, and those of the latter strongly, deformed. There was, however, as yet no experimental criterion to fix a boundary between the two (*cf.* also the remark on p. 408).

Thus a *principle* of the absolute absence of molecules in solutions of strong electrolytes was not justified by experimental facts and was opposed to the thermodynamically assured distribution law.

**Professor A. W. Porter** inquired whether Lorentz's equation for refractivity did not assume that there was mutual action between any ion and the surrounding medium (consisting in part of ions). In such a case he would not expect an additive law to hold good. This constituted an essential difference between Lorentz's and Drude's equations.

It must also be remembered that Lorentz assumes a special value for this action. The question had been very thoroughly discussed by Natanson in the Bulletin of the Academy of Sciences of Cracovie, 1907. He (Professor Porter) also mentioned that measurements made in his laboratory by Dr. Percy Phillips upon carbon dioxide<sup>4</sup> indicated that Lorentz's law did not appear to be exactly true even for a gas. The *reciprocal* of Lorentz's constant was found to vary according to a linear law with the *square* of the density; changing for blue light from about 6.50 at low densities to 6.55 when the square of the density was 0.5. These results would be obtained if the effects of a polarisation on the field were not  $\frac{4\pi P}{3}$  but  $\frac{4\pi P}{3} + \sigma P$  where  $\sigma$  was proportional to the density.

In the deviations produced in the above way from the straight line law there was no idea of any alterations of the positions of the electrons in any one atom or other form of strain in the atom. It was this modification of the surrounding medium which was taken into account. This could with very little doubt be represented as a modification of the dielectric constant of the medium.

**Professor Fajans** replied that in the consideration of refraction one must distinguish between two kinds of mutual action between the individual particles of a system. The first was a consequence of the polarisation of the particles in the electric field of the light wave; the Lorentz formula attempted to take account of the reciprocal effect of these. The other, which was here of special interest, occurred in the deforming action of the field of the particles also in the dark, so that the wave struck particles which were already deformed; this should be made evident in deviation from additivity in the Lorentz refraction. Of course the Lorentz formula was based on certain assumptions and was derived strictly for a system consisting only of particles of the same kind. He agreed therefore with Professor Porter that one could not *a priori* expect with

<sup>3</sup> Bjerrum, *Erg. d. exakt. Naturw.*, 1926, 5, 140.

<sup>4</sup> Roy. Soc. Proc., A, 97, 1920, 225.

certainty that in a complicated system the Lorentz refraction would show strict additivity without the action of the second kind. By systematic investigation of the actual deviations from additivity occurring in most cases it ought to be possible to decide whether these were to be traced back to these deformation actions or to an insufficiency of the Lorentz formula. With regard to the large deviations which followed such simple rules (as were made evident in Fig. 1 or Table I and also found for many other combinations of ions in crystals), there would seem to be no doubt that they might be regarded for the greater part as manifestations of a real "dark effect." The much smaller deviations from additivity in the case of concentrated solutions (Fig. 2) were accounted for similarly by the rules which had been discussed; the extension of the experimental results which was to be expected shortly would probably bring complete clarity there.

But even in the approach of neutral gas molecules deformation effects were to be expected, and Debye<sup>5</sup> had, as a matter of fact, explained the Van der Waals' forces by means of the polarisation of the gas molecules by the electric field of their neighbours. In the work of Fajans and Joos<sup>6</sup> it was also indicated that the decrease of the Lorentz refraction obtained in numerous cases in the transition from a gas to a liquid could possibly be explained in that way. Certainty, however, as to whether the manifestation of the effects might not be due simply to an incompleteness of the Lorentz formula would also only be obtained by a systematic investigation of the dependance of these effects on the size of the electric moment and polarisability of the particular molecule. It must be mentioned, however, that the exact and interesting measurements by Phillips on carbon dioxide referred to by Professor Porter were consistent with such an explanation as a polarisation effect. Phillips found a lowering from 6.68 to 6.62, *i.e.* a difference of 0.06 (for 5461 Å), when recalculated for molecular refractivity in the transition from low pressures to a density of 0.737 corresponding to a molecular volume of 59.7 c.c. The corresponding lowering in the union of the free ions  $\text{Rb}^+$  and  $\text{I}^-$  to solid  $\text{RbI}$  (molecular volume 59.8 c.c.) had a value of 1.1 units of refraction (*cf.* Fig. 1). The first was therefore much smaller. That could be understood because the dipolar molecule  $\text{CO}_2$  had a much weaker field than the ion  $\text{Rb}^+$  and a smaller polarisability than  $\text{I}^-$ . The proportionality of the effect with the square of the density mentioned by Professor Porter meant that it was inversely proportional to the 6th power of the average distance between the molecules. It was not unexpected that this power in the case of the action of dipolar molecules should be higher than the 4th power obtained in the action of ions.

**Mr. F. I. G. Rawlins** (*communicated*) said that the position as Professor Fajans stated it seemed so well defined that he ventured to look at some of the implications of his paper in their bearing upon other physical phenomena.

For lucidity, the points might be taken as they occurred in the summary.

1. *The relationship  $\Delta R \cdot r^4 = k$ .*—Apart altogether from the theoretical basis of this expression, the quantitative results obtained from it were perhaps not quite convincing. Since it occurred to the 4th power, it seemed somewhat fortuitous that  $k_1$  came out so well. Thus, the Geiger-Scheel Handbook (1926, 22, p. 500) gave  $r$  for  $\text{LiI}$  = 3.007 (not 3.025), and minor differences for some of the others: not points of great consequence in themselves, but important in the application of a formula involving a 4th power.

<sup>5</sup> *Physik. Z.*, 1920, 21, 178.

<sup>6</sup> *Z. Physik*, 1924, 23, 40.

Even with the refined technique now available for the determination of inter-ionic distances, one might perhaps be permitted to question whether it were yet justifiable to rely upon them to the extent demanded for the constancy of  $k$  in this equation.

2. In connection with Professor Fajans' suggestion of an analogy between concentration and crystal building (especially in virtue of the importance of ionic "size") it might be interesting to notice what might be expected to happen on the theory of Heckmann and others<sup>7</sup> relating to the kind of lattice which would arise under given conditions.

Thus, the introduction of polarisation—more especially of the type associated within poles of high order—made possible the appearance of such forms of lattice as the molecular, radical, and "stratified" varieties. In a word, the stability was determined by  $\alpha$ , the deformability, or moment per unit field (corresponding to  $\frac{3}{4\pi N} \cdot R$  in Professor Fajans' notation).

Recent work of Simon and Simon<sup>8</sup> left little room for doubt that solid HCl had a molecular lattice, which fitted in admirably with Professor Fajans' views on the behaviour of this substance in solution.

He hoped that Professor Fajans could give more information upon such compounds as  $\text{CaCO}_3$  (radical lattice) or  $\text{CdI}_2$  (stratified lattice).

Meanwhile, matters might not be so straightforward as the considerations just indicated for HCl might lead them to suppose, when attempts were made to correlate properties between crystal, solution, and gas.

Professor Fajans referred to the HCl molecule as having a structure "more closely allied to that of non-polar compounds than to that of typical salts." However this might be in the crystal, HCl (gas) would appear to be an almost perfect example of a polar substance when looked at from the point of view of specific heats, band-spectra, and the new mechanics. He would not go into the evidence as it had been thoroughly sifted by Van Vleck.<sup>9</sup>

3. The existence of direct ionic contact in solution raised immediately an interesting point. Reinkober<sup>10</sup> had investigated the infra-red spectrum of  $\text{NH}_4\text{Cl}$  (conc.) in water. The characteristic frequency (internal oscillation) of the  $\text{NH}_4$  ion occurred at a shorter wave-length in solution than in the solid—the opposite of the usual effect. Since it was usually accepted that internal vibrations were influenced by the other ion (Cl in this case), it might be inferred that the dielectric was playing some important part, suggesting that actual contact was absent.

**Professor K. Fajans** (*communicated*) said in reply :—

1. The values of the lattice distance  $r$  used in the proof of the 4th power relationship in Table II. were taken from the latest summary of Goldschmidt.<sup>11</sup> For LiI the value of  $3.025 \pm 0.02$  was given. The earlier values obtained from X-ray measurements lay between  $3.00$ <sup>12</sup> and  $3.03$ ,<sup>13</sup> whilst the intermediate value of  $3.007$  given by Mr. Rawlins was calculated from a density determination of Baxter and Wallace (1916)<sup>14</sup>. If in Table II. one used instead of  $3.025$  the value which differed most greatly from it, *viz.*  $3.00$ , then one would obtain for  $K = \Delta R \cdot r^4$ , instead

<sup>7</sup> See Born's *Atomdynamik*, Part II., Chap. VII.

<sup>8</sup> *Z. Physik.*, 1924, **21**, 168.

<sup>9</sup> *Physical Review*, 1926, **28**, 980.

<sup>10</sup> *Z. Physik.*, 1926, **35**, 179.

<sup>11</sup> *Norske Vidensk. Akad.*, 1926, **8**, pp. 71, 145.

<sup>12</sup> Ott, *Physik. Z.*, 1923, **24**, 209.

<sup>13</sup> Posnjak and Wyckoff, *Wash. Acad.*, 1922, **12**, 248.

<sup>14</sup> Fajans and Grimm, *Z. Physik.*, 1920, **2**, 299.

of 290, the value 280, which was still in quite satisfactory agreement with the value 291 for NaI. The value of  $r$  for NaI obtained from the most recent X-ray measurements<sup>15</sup> was 3.231 and that from Baxter's density determination 3.232. If one took as being correct the value 3.00 for LiI and the  $\Delta R$  values of Table II., which of course had a certain amount of error attached to them, then one would get the 3.5th power instead of the 4th. The conclusions from the calculations in section 8a would not thereby be altered in the slightest. The theoretical meaning of the 4th power might well depend upon the fact that the potential energy of one dipole induced by an ion on another varies in inverse proportion to the 4th power of their distance apart.<sup>16</sup>

2. In order to avoid all misapprehension he (Professor Fajans) wished to emphasise clearly that he did not believe that in general the distribution of the ions in solution was the same as that in the lattice. The absurd result of the calculation made on that assumption in the case of LiCl (section 8a) proved the exact opposite. With regard to the connection between polarisation of the ions and lattice type the question had been thoroughly discussed by Hund<sup>17</sup> and Goldschmidt.<sup>18</sup>

It sufficed at that stage to indicate a connection between lattice type and behaviour in solution. The fact that  $\text{CO}_3$  behaved as a radical ion and was not split up into atom ions by the cations in the lattice or by hydration forces in the solution depended on the strong polarisation of the O ions by means of the  $\text{C}^{4+}$ ; one must consider the  $\text{CO}_3$  ion as well as other complex ions ( $\text{SO}_4$ ,  $\text{ClO}_4$ , etc.) as being more closely allied to non-polar compounds than to compounds built up of ions.<sup>19</sup>

The strong polarisation of the  $\text{I}^-$  ion by the  $\text{Cd}^{++}$  ion, which did not belong to the inert gas type, was not only made manifest in the formation of a stratified lattice, but was also evident in the fact that  $\text{CdI}_2$  boiled relatively easily and in solution constituted an electrolyte of only medium strength with a strong tendency to form complex ions.

Of course, the HCl molecule as well as the above-mentioned complex ions had a certain polarity, which made allowance for the properties mentioned by Mr. Rawlins. That HCl, however, was actually more like a non-polar compound than a typical salt was shown conclusively by the fact that the dipole moment of HCl, if it were to consist of separate ions, ought on the basis of its nuclear distance of 1.25 Å.<sup>20</sup> to have the value  $5.96 \times 10^{-18}$  e.s.u. whereas actually the moment was only  $1.03 \times 10^{-18}$ .

3. The observations of Reinkober were in no way inconsistent with his (Professor Fajan's) conclusions. The displacement of the frequency of internal oscillation of an ion in the transition from the solid state to the solution was dependent on the fact that with strong electrolytes, even in concentrated solutions, a very considerable proportion of the ions were separated from one another by molecules of the solvent and thus withdrawn from the influence of their partners. The effect which occurred was opposite from the usual, because, as Reinkober himself emphasised, the previously observed displacements towards a longer wave-length were confined to the vibrations of anions (e.g.  $\text{SO}_4^{--}$ ), whereas Reinkober investigated that of the cation  $\text{NH}_4^+$ , the vibration of which was displaced toward the shorter wave-length by the solution of the  $\text{NH}_4\text{Cl}$ . This formed a good

<sup>15</sup> Davey, *Physical Rev.*, 1923, 21, 143.

<sup>16</sup> Cf. e.g. Born and Heisenberg, *Z. Physik*, 1927, 23, 404.

<sup>17</sup> *Z. Physik.*, 1925, 34, 833.

<sup>18</sup> *Ber.*, 1927, 60, 1263.

<sup>19</sup> Cf. the papers mentioned in foot-notes 1 and 2 of page 357.

<sup>20</sup> Cf. *Geiger Scheel Handbook*, 1926, 22, 478, 486.

parallel to the opposite action of the ions on one another which was found in the case of refraction. A contradiction of the direct contact between a part of the ions in solution would only then be found, if by concentrating the solution there were to appear for a definite frequency a displacement opposite to that found for the transition solution-solid. The accuracy of the particular absorption measurements in the infra-red was, however, with  $\text{NH}_4\text{Cl}$  too small to establish any sort of influence of the concentration.

## ELECTROLYTIC TRANSFERENCE OF WATER, TRUE TRANSFERENCE NUMBERS, IONIC MOBILITIES AND WATER SHEATHS OF THE IONS.

By H. REMY.

(TRANSLATED BY H. BORNES.)

### I. Electrolytic Transference of Water and True Transference Numbers.

Recent determinations of the transference of water for a large number of electrolytes in normal aqueous solutions enable us to calculate the true transference numbers in normal solutions of these electrolytes. The equation used is

$$w_e = n_e - cW_e \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $W_e$  indicates the electrolytic transference of water,  $w_e$  the true transference number and  $n_e$  the experimental Hittorf transference number, all for the electrolyte concentration  $c$  expressed in equivalents per mol. The true transference numbers (molecules of water per ion) of Table I. have been calculated from this formula on the basis of the Hittorf numbers given in the fourth column. The respective Hittorf values have, for the chlorides, been taken from the tables of Kohlrausch;<sup>1</sup> for the iodides they have been determined by myself and A. Kuhlcke; for the bromides they have been deduced from the corresponding chloride values by the aid of the formula,

$$n_{\text{bromide}} = 1.06 n_{\text{chloride}} \frac{\Lambda_{\text{chloride}}}{\Lambda_{\text{bromide}}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $n$  is again the Hittorf number and  $\Lambda$  the equivalent conductivity. Equation (2) is derived by the following consideration: the apparent mobility  $\lambda_A$  of the ion A of the electrolyte AB at a given concentration is defined by

$$\lambda_A = n \cdot \Lambda_{AB} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $n$  is the transference number of the ion A and  $\Lambda_{AB}$  the equivalent conductivity, both for the electrolyte AB. In the case of a chloride and a bromide containing the same kation:

$$\frac{n_{\text{bromide}}}{n_{\text{chloride}}} = \frac{\lambda_{\text{Br}}}{\lambda_{\text{Cl}}} \cdot \frac{\Lambda_{\text{chloride}}}{\Lambda_{\text{bromide}}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

<sup>1</sup> F. Kohlrausch and L. Holborn, "Leitvermögen der Elektrolyte," 2nd edition, 1916.

TABLE I.

WATER TRANSFERENCE AND TRUE TRANSFERENCE NUMBER IN NORMAL SOLUTIONS OF INORGANIC ELECTROLYTES.

Electrolyte.	Water Transference.	Observer.	Hittorf Transference Number.	True Transference Number. Mean.	Transference Number at Infinite Dilution.	
HCl	0.28	B.	0.156(0.158)	0.151(0.153)	0.172	
"	0.37	R. & M.	0.156	0.149		
LiCl	1.5	W.	0.739(0.724)	0.711(0.696)	0.662	
"	1.4	R. & M.	0.739	0.713		
"	1.6	R. & R.	0.739	0.710		
NaCl	0.81	W.	0.637(0.634)	0.622(0.617)	0.601	
"	0.82	W. & M.	0.637(0.638)	0.622(0.626)		
"	0.85	R.	0.637	0.621		
"	1.0	R. & M.	0.637	0.619		
"	1.4	R. & R.	0.637	0.611		
KCl	0.60	W.	0.514(0.518)	0.503(0.505)	0.503	
"	0.57	R.	0.514	0.503		
"	0.47	R. & M.	0.514	0.505		
"	0.47	R. & R.	0.514	0.505		
CsCl	0.36	W. & M.	0.515	0.509	0.509	0.491
NH <sub>4</sub> Cl	0.55	R. & M.	0.514	0.504	0.501	0.506
"	0.87	R. & R.	0.514	0.498		
$\frac{1}{2}$ MgCl <sub>2</sub>	- 0.08	R. & M.	0.709	0.710		0.593
$\frac{1}{2}$ CaCl <sub>2</sub>	- 0.20	"	0.686	0.690		0.562
$\frac{1}{2}$ SrCl <sub>2</sub>	- 0.97	"	0.686	0.704		0.562
$\frac{1}{2}$ BaCl <sub>2</sub>	- 1.23	"	0.640	0.663		0.544
HBr	0.61	R. & M.	0.164	0.153		0.177
NaBr	2.2	"	0.642	0.601		0.608
KBr	0.84	"	0.532	0.516		0.511
$\frac{1}{2}$ MgBr <sub>2</sub>	0.30	"	0.709	0.704		0.600
$\frac{1}{2}$ CaBr <sub>2</sub>	- 0.17	"	0.684	0.687		0.570
$\frac{1}{2}$ SrBr <sub>2</sub>	- 0.24	"	0.684	0.688		0.570
$\frac{1}{2}$ BaBr <sub>2</sub>	- 0.84	"	0.643	0.659		0.551
$\frac{1}{2}$ MgI <sub>2</sub>	- 0.67	R. & R.	0.670	0.682		0.578
$\frac{1}{2}$ CaI <sub>2</sub>	- 0.92	"	0.637	0.654		0.566
$\frac{1}{2}$ SrI <sub>2</sub>	- 0.75	"	0.636	0.650		0.566
$\frac{1}{2}$ BaI <sub>2</sub>	- 0.85	"	0.609	0.625		0.547

B.: Buchböck, *Z. physik. Chem.* (1906), 55, 563; W.: Washburn, *Z. physik. Chem.* (1909), 66, 513; *J. Amer. Chem. Soc.* (1909), 31, 322; W. & M.: Washburn & Millard, *J. Amer. Chem. Soc.* (1915), 37, 694; R.: Remy, *Z. physik. Chem.* (1915), 89, 529; R. & M.: Remy & Manegold, *Z. physik. Chem.* (1925), 118, 161; R. & R.: Remy & Reisener, *Z. physik. Chem.* (1926), 124, 394.

Kohlrausch's tables of ionic mobilities at different concentrations of the electrolyte give the following mobility ratios at 18°:

	$l_{Br} : l_{Cl}$	$l_{I} : l_{Cl}$
in $N/10000$ solution	= 1.032	= 1.011
$N/1000$ "	= 1.033	= 1.014
$N/100$ "	= 1.036	= 1.019
$N/10$ "	= 1.059	= 1.054.

Accepting the figure 1.054 as approximately correct for the ratio of the apparent mobility of the iodine as well as the chloride ions in normal solutions, and calculating the transference numbers of the iodides of the alkaline-earth metals from those of the chlorides by a formula analogous to (4), we find

$$n_{\text{BaI}_2} = 0.611 \quad n_{\text{CaI}_2} = 0.646 \quad n_{\text{MgI}_2} = 0.670,$$

the experimental values are

$$0.609 \pm 0.002 \quad 0.637 \pm 0.002 \quad 0.670 \pm 0.003$$

The agreement is sufficiently satisfactory to admit of a similar deduction for the transference numbers of the bromides, reliable experimental data for which are not yet available. The experimental value of the transference number for strontium iodide is almost the same as that for calcium iodide and, according to Kohlrausch, the mobilities of the strontium and calcium ions hardly differ from one another to any appreciable extent; we have therefore assumed the experimental transference numbers of strontium bromide and chloride to have the values of the respective calcium salts.

Determinations of the electrolytic transference of water have been effected by Buchböck and Washburn by the Nernst method of an indifferent (stationary) reference substance, by Remy by the diaphragm method of mechanical fixation of the centre. The diaphragm used consisted in the earlier work (1915) of gelatin, in the recent work of parchment paper. Of the earlier results only the data for solutions of KCl and NaCl have been entered in the Table, because with the other electrolytes the transference number, and hence the water transport, was too much affected by the presence of the gelatin.<sup>2</sup> The interposition of a parchment diaphragm in the current path is, on the other hand, according to W. Bein<sup>3</sup> and W. Hittorf,<sup>4</sup> of little influence in diluted solutions especially of alkali salts. Electro-osmosis plays, with parchment paper in normal electrolyte solutions, so small a part by comparison with the transference of water that it may for the present be disregarded. The discrepancies between the true transference numbers as calculated from water transferences observed by different authors are small. The methods now available for the determination of the electrolytic transference of water are therefore sufficiently accurate for the calculation of true transference numbers by equation (1), provided that the experimental data be exact.<sup>5</sup>

The figures enclosed in brackets in Table I. have been obtained directly from the experiments of the investigators stated, who conducted the determination of the water transference by the method of the indifferent reference substance. Those of Washburn do not, however, concern pure aqueous solutions and cannot be considered as fully equivalent to such data. Buchböck's transference number for hydrogen chloride, also, is not quite reliable; he worked only with one intermediate layer. The magnitude of water transference is itself not quite independent of the presence of the reference substance in the solution. Buchböck has eliminated this influence by calculation; in Washburn's figures it may be neglected owing to the small concentration of reference substance. It will hence be admissible to make

<sup>2</sup> As regards the influence of gelatin-addition on transference-number see Richter, *Z. physik. Chem.*, 1912, 80, 449; Ferguson and France, *J. Amer. Chem. Soc.*, 1921, 43, 2161; France and Moran, *ibid.*, 1924, 46, 19.

<sup>3</sup> *Z. physik. Chem.*, 1898, 28, 439.

<sup>4</sup> *Z. physik. Chem.*, 1902, 39, 613; 1903, 43, 237.

<sup>5</sup> Remy, *ibid.*, 1925, 118, 161; Remy and Reisener, 1926, 124, 41.

use of these data for the calculations by formula (1) as well as of those obtained by other methods with pure aqueous solutions.

The figures, in the last column of Table I., for the transference numbers at infinite dilution, have been calculated from Kohlrausch's ionic mobilities. The true transference number of potassium chloride is in practical accord with the transference of this substance at infinite dilution. For other substances of the type KCl we have: Hittorf transference number > true transference number > transference number at infinite dilution. But for the halogen hydrides and for the halides of the alkaline earth metals (with the exception of  $\text{MgBr}_2$ ) the true transference numbers differ from the transference numbers at infinite dilution more strongly even than the experimental transference numbers.

## II. Transference Numbers and Ionic Mobilities.

When we substitute in equation (3) the true transference number  $w$  for the experimental value  $n$ , we find

$$\lambda_A^w = w\Lambda_{AB} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This relation defines the quantity  $\lambda_A^w$  which we call the "true mobility" of the ion  $A^0$  in analogy to the true transference number. By combinations of (5) with (1) and (3) we obtain further

$$\lambda_A^w = \lambda_A - \Lambda_{AB} \cdot c \cdot W_c \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The true mobility is free from the accidental component of the apparent mobility depending upon the method of measurement.

Table II. provides a comparison of the apparent and true mobilities  $\lambda$  and  $\lambda^w$  of the common ion in normal solutions of several series of cognate electrolytes; the equivalent conductivity values  $\Lambda$  used in the calculations by the aid of equations (3) and (5) are likewise entered. It will be seen that the true mobilities are as much influenced, as are the apparent mobilities, by the nature of the ion which is not common to the compounds; when in comparing two electrolytes which have one ion in common and the two other ions of which are homologous, we multiply the mobility by the viscosity  $\eta$  (or specific viscosity  $\eta_s$ ), however, we obtain values which are in better accord for the true mobilities than for the apparent mobilities.

For the common ion of each pair of electrolytes in the ten cases summarised in Table II. the discrepancies in the true mobilities amount in the mean to 4.6 per cent., those in the apparent mobilities to 4.3 per cent. For the product  $\lambda\eta$  (or  $\lambda\eta_s$ ) the mean discrepancy is 3.8 per cent., for the product  $\lambda^w\eta$  (or  $\lambda^w\eta_s$ ), however, it is only 2.6 per cent. It should be noted that the viscosities are not in all cases referred to the same temperature (18°) as the mobilities; if we limit ourselves to the cases in which the viscosities were also determined at 18° the mean discrepancy for the product  $\lambda^w\eta$  (or  $\lambda^w\eta_s$ ) falls to 2.0 per cent. The quotient: mobility/coefficient of conductivity,  $f_A = \Lambda/\Lambda_\infty$ , likewise shows smaller fluctuations for the true than for the apparent mobilities; in the ten cases tabulated the former amounts on average to 2.2 per cent., the latter to 2.9 per cent.

The examples given justify the hope that the adoption of true mobilities would facilitate progress in the study of solutions of moderate concentration. Data for more diluted solutions, e.g.  $N/10$ , would still more be desirable.

<sup>6</sup> The term "true mobility" is occasionally used to indicate the quotient of mobility by degree of dissociation or coefficient of conductivity. This quotient should, however, rather be called "specific mobility," if a special term be needed. Logically we should then distinguish between apparent and true specific mobility.

For the present the determinations of the water transference by the diaphragm method are not sufficiently reliable in dilute solutions; it is difficult to eliminate the electro-osmotic effect superposed upon the transference.

TABLE II.  
APPARENT AND TRUE IONIC MOBILITY IN NORMAL SOLUTIONS.

Electrolyte.	$\Lambda$ .	$\eta$ or $\eta_s$ .	$f_{\Lambda} = \frac{\Lambda}{\Lambda_{\infty}}$	$\lambda$ .	$\lambda^w$ .	$\frac{\lambda \cdot \eta}{\lambda \cdot \eta_s}$ .	$\frac{\lambda^w \cdot \eta}{\lambda^w \cdot \eta_s}$ .	$\frac{\lambda}{f_{\Lambda}}$ .	$\frac{\lambda^w}{f_{\Lambda}}$ .
KCl	98.3	$\eta^{18^\circ}$ 0.98207	0.756	50.53	49.54	49.62	48.65	66.84	65.53
NaCl	74.3	1.0858	0.682	47.33	45.99	51.39	49.94	69.40	67.43
LiCl	63.4	1.1498	0.642	46.85	45.08	53.87	51.83	72.98	70.22
CaCl <sub>2</sub>	67.5	1.1501	0.579	46.31	46.58	53.26	53.57	79.98	80.45
MgCl <sub>2</sub>	61.5	1.2126	0.556	43.60	43.67	52.87	52.95	78.42	78.54
KCl	98.3	$\eta_s^{18^\circ}$ 0.01055 <sup>8</sup>	0.756	50.53	49.54	0.533	0.523	66.84	65.53
NaCl	74.3	0.0116	0.682	47.33	45.99	0.549	0.533	69.40	67.43
KBr	100.6	0.01031	0.764	53.52	51.91	0.552	0.535	70.05	67.95
NaBr	78.1	0.01145	0.707	50.14	46.94	0.574	0.537	70.92	66.39
KCl	98.3	$\eta^{20^\circ}$ 0.010095 <sup>9</sup>	0.756	50.53	49.54	0.510	0.500	66.84	65.53
NaCl	74.3	0.011225	0.682	47.33	45.99	0.531	0.516	69.40	67.43
BaCl <sub>2</sub>	70.1	0.013156	0.582	44.86	46.48	0.590	0.611	77.08	79.86
CaCl <sub>2</sub>	67.5	0.013320	0.579	46.31	46.58	0.617	0.620	79.98	80.45
MgCl <sub>2</sub>	61.5	0.013503	0.556	43.60	43.67	0.589	0.590	78.42	78.54
KCl	98.3	$\eta_s^{15^\circ}$ 0.622 <sup>10</sup>	0.756	47.77	48.76	29.71	30.33	63.19	64.50
KBr	100.6	0.601	0.764	47.08	48.69	28.30	29.26	61.62	63.73
HCl	301	0.667	0.791	25.40	25.59	16.94	17.07	32.11	32.35
HBr	301	0.650	0.792	25.16	25.49	16.35	16.57	31.77	32.18

### III. Water Sheaths of the Ions.

The electrolytic transference of water  $W$  is a function of the water sheaths<sup>11</sup> of the anion and kation  $h_A$  and  $h_K$ , and of the true transference numbers  $w$  and  $(1 - w)$  according to

$$W = (1 - w)h_K - wh_A \quad (7)$$

Determination of the electrolytic transport of water hence admits in the first instance only of conclusions concerning the relative magnitude of the water

<sup>7</sup> E. Grüneisen, *Wiss. Abh. Phys.-Techn., Reich.* IV. (1918), 237. Viscosities are referred to water at 18°.

<sup>8</sup> F. H. Getman, *J. Am. Chem. Soc.* (1908), 30, 721.

<sup>9</sup> K. Mützel, *Wied. Ann.* (1891), 43, 15.

<sup>10</sup> W. W. Tayler and C. Ranken, *Proc. Royal Soc., Edinburgh* XXV. (1904), 231. Viscosities are referred to water at 0°.

<sup>11</sup> Since hydrates are assumed to contain their water chemically bound (whilst leaving open the question as to whether the water moving with the ions in electrolysis is essentially in chemical combination, or is essentially if not predominantly, carried along in the sense of Born and Lorenz and of Debye and Hückel), we speak of this water as a (possibly fictitious) envelope and do not use the term hydration; see Remy, *Z. physik. Chem.*, 1915, 89, 469.



TABLE III.

WATER SHEATHS OF INORGANIC IONS IN NORMAL SOLUTIONS.

Water sheath of Cl<sup>-</sup>-Ion = 3H<sub>2</sub>O.,, ,, Br<sup>-</sup>-Ion = 2.1H<sub>2</sub>O.,, ,, I<sup>-</sup>-Ion = 3.7H<sub>2</sub>O.

Ion.	Water Sheaths, Calculated from Water Transference in		
	Chlorides.	Bromides.	Iodides.
H <sup>+</sup>	0.9	1.1	—
Li <sup>+</sup>	12.6	—	—
Na <sup>+</sup>	7.4	8.8	—
K <sup>+</sup>	4.1	4.0	—
Cs <sup>+</sup>	3.8	—	—
[NH <sub>4</sub> ] <sup>+</sup>	4.4	—	—
[NH <sub>3</sub> OH] <sup>+</sup>	2.8	—	—
Mg <sup>2+</sup>	14.1	11.9	11.7
Ca <sup>2+</sup>	12.1	8.1	8.7
Sr <sup>2+</sup>	7.7	7.7	9.5
Ba <sup>2+</sup>	4.5	3.1	(7.8)

but the number of observations is still small. The data leave no doubt, however, that the water sheath of the iodine-ion is greater than that of the bromine-ion. Further, if we accept the value 3.71 for the water sheath of the iodine-ion, the resulting sheaths for the ions of the alkaline-earth metals except barium ion, agree with those derived from the chloride and bromide experiments.

TABLE IV.

WATER SHEATHS OF ORGANIC IONS IN NORMAL SOLUTIONS.

Ion Water sheath	[CH <sub>3</sub> .NH <sub>3</sub> ] <sup>+</sup>	[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup>	[(CH <sub>3</sub> ) <sub>3</sub> NH] <sup>+</sup>	[(CH <sub>3</sub> ) <sub>4</sub> N] <sup>+</sup>
	2.4	3.9	4.4	4.6
Ion Water sheath	[C <sub>2</sub> H <sub>5</sub> .NH <sub>2</sub> ] <sup>+</sup>		[n-C <sub>3</sub> H <sub>7</sub> .NH <sub>3</sub> ] <sup>+</sup>	
	4.3		5.5	

Finally we summarise in Table IV. the values for the water sheaths of some organic compounds calculated from quite recent experiments.<sup>13</sup> The transference numbers of these electrolytes not being known for normal solutions, we had to make use of the ionic mobilities found for N/32 solutions. The values of Table IV. are therefore to be regarded as preliminary. The possibility of basing calculations upon absolute values of the water sheath will, it is hoped, also enable us to approach the problem, whether the water sheaths stated in Tables III. and IV. represent chemically-bound water, or whether the water is merely carried along by some electrodynamic effect, such that the moving ions possess "fictitious water sheaths," whilst there would be no hydration of the ions at rest.

### Summary.

The available data upon the electrolytic transference of water in normal aqueous solutions of inorganic electrolytes are tabulated and utilised for the calculation of the true transference numbers.

The product of the thus calculated true mobility of an ion in normal solution and its viscosity changes, when we pass from one solution to another

of homologous type, much less than when we take the product of the apparent mobility and viscosity. This applies similarly to the quotient of mobility over coefficient of conductivity.

Starting from water transference in solutions of organic electrolytes with large kations, not carrying water envelopes, we arrive at absolute values for the water sheaths of the ions. The absolute amounts of the water carried have been calculated from the measurements of water transferences for some inorganic and organic ions.

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## IONIC MOBILITIES IN NON-AQUEOUS SOLVENTS.

BY HERMANN ULICH, ROSTOCK.

(TRANSLATED BY H. BORN.)

Our knowledge of ionic mobilities in non-aqueous solvents (*i.e.*, mobilities at infinite dilution of the dissolved salt, and hence, strictly speaking, limiting mobilities) is still very defective, although such knowledge would be valuable in various respects. Experimental measurements of this mobility have only been attempted in a few cases, and the results differ considerably. The difficulties to be overcome are great and are doubled when the methods available for measurements in water as solvent are applied; the uncertainties affecting the limiting conductivities and the transference numbers are superposed. The transference numbers are moreover dependent upon concentration. That influence, appreciable in water, becomes much more marked in solvents of low dielectric constant, owing to the enhanced effects of interionic forces and of complex formation. Thus in general only transference determinations (or direct mobility measurements by observing the boundary displacement) at very high dilution will be available for our purposes. That the want of accord in the values of the ionic mobilities of various authorities is mainly to be ascribed to the uncertainty of the transference numbers is evidenced by the tables of Walden<sup>1</sup> and of other workers.

The researches of Walden on the relation between conductivity and viscosity have opened up a new way for the determination of limiting mobilities in non-aqueous solvents. The method requires only knowledge of the limiting conductivity. The method was already applied by Walden in his papers of 1920 and 1924, on ionic mobilities; a secure basis for its application was only established by later researches.<sup>2</sup> The relation recognised by Walden in 1906, that the product of limiting conductivity  $\Lambda_{\infty}$  and viscosity of the solvent  $\eta$  is for a given salt constant and independent of the solvent proved quite correct and generally valid for salts which consist of large ions presumably not admitting of solvation on account of their size. For such ions the same relation must hold for the

<sup>1</sup> Walden, *Leitvermögen der Elektrolyte*, I., Leipzig, 1924; *Elektrochemie nicht-wässriger Lösungen*, Leipzig, 1924.

<sup>2</sup> Walden and Ulich, *Z. physikal. Chem.*, 1923, 107, 219; 1925, 114, 297. Walden, Ulich, and Busch, *ibid.*, 1926, 113, 429; Ulich, *Beweglichkeit der elektrolytischen Ionen*, *Fortschritte der Chemie, Physik u. physikal. Chemie*, edited by A. Eucken, Berlin: Gebr. Borntraeger, 1926, 18, No. 10; this paper will be quoted as *Fort.*

ionic mobility  $l$  and the viscosity  $\eta$ , and it is only necessary to determine the product  $l\eta$  for such an ion in water, in order to be able to predict the mobilities in all other media. It was important to prove that for these large ions, as distinct from many others, the  $l\eta$ -product in water is also constant with respect to temperature and is indeed a quantity depending only upon the kind of ion (Walden and Ulich, *loc. cit.*).

The substance chosen for starting the calculations was the large and symmetrical ion  $\text{N}(\text{C}_2\text{H}_5)_4^+$  of tetraethylammonium salts, the mobility of which in water was calculated from the measurements of several experimenters. The mean resulting value was  $l\eta = 0.295$ . Measurements on these salts having been conducted in numerous solvents, the data could be used for calculating the mobilities of other ions in various solvents. Tables I. and II. summarise these results (further details will be found in the *Fort.*). Extrapolations of the basal limiting conductivities were made on the square root law.

The accuracy of the ionic mobilities given depends upon the accuracy of the limiting conductivities, which can not always be considered high. The reliability was further reduced by the fact that any errors in the  $\Lambda_\infty$  values of the salt containing the  $\text{N}(\text{C}_2\text{H}_5)_4^+$  ion would recur in all the ions, and that held again for the occasionally large uncertainty of the viscosity coefficient. In very unfavourable cases the error may attain the order of magnitude of 10 per cent.; on the other hand the values in the solvents ethyl and methyl alcohol and acetone may be regarded as particularly reliable. It should be noted that the  $l\eta$ -product may be considered as constant with respect to temperature in all the non-aqueous solvents in question (*cf. Fort.*). The reliance placed upon the method and the results obtained is strengthened by the fact that in some cases approximate constancy of the  $l\eta$ -product was observed; that could not be merely accidental. The cases concerned the ions  $\text{N}(\text{CH}_3)_4^+$ ,  $\text{N}(\text{C}_3\text{H}_7)_4^+$ ,  $\text{N}(\text{C}_5\text{H}_{11})_4^+$ , picrate<sup>-</sup>, styphnate<sup>-</sup>, as well as  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CNS}^-$ , (*cf. Fort.*).

Comparative transference numbers could only be obtained in methyl- and ethyl-alcohol. As regards methyl-alcohol the values found by Nonhebel and Hartley<sup>3</sup> for solutions of HCl are of the greatest importance; they found for very dilute solutions:  $n_{\text{H}^+} = 0.735 \pm 0.005$ , whilst we calculate 0.733. The ionic mobilities of Frazer and Hartley,<sup>4</sup> based upon these transference experiments, are practically identical with those I have calculated by an entirely different method. There is also good agreement for solutions in ethyl alcohol. In these Harned and Fleysher (1925) found for diluted HCl  $n_{\text{H}^+} = 0.738$  and 0.752, Hardman and Lapworth (1912) 0.76, Lapworth (1915) 0.69; we calculated 0.741. Measurements of transference numbers in solutions of  $\text{AgNO}_3$ , made between 1901 and 1916 by six investigators, are likewise in encouraging agreement; the single values  $n_{\text{NO}_3^-}$  varied between 0.594 and 0.616, the mean was 0.602; our calculation yielded 0.605. We could, of course, also quote deviating figures; but the best values recorded come close to our calculations, and that justifies our method.

The consideration of our ionic mobilities leads to the following conclusions which are theoretically noteworthy.

1. The Walden relation ( $l\eta$  is constant for any solvent) is valid in the cases stated.

2. The sequence of mobilities is, for the alkali series, the same for water and the other solvents, that is to say, it is the opposite of what one might

<sup>3</sup> *Phil. Mag.*, 1925, 1, 729.

<sup>4</sup> *Proc. Roy. Soc.*, 1925, A, 109, 351.

TABLE I.—IONIC MOBILITIES AT 25° C.

Solvent.	D.C.	100 $\eta$ .	$N(C_2H_5)_4^+$ .	$N(CH_3)_4^+$ .	Na <sup>+</sup> .	K <sup>+</sup> .	Cl <sup>-</sup> .	Br <sup>-</sup> .	I <sup>-</sup> .	CNS <sup>-</sup> .
Water, H <sub>2</sub> O . . . . .	79	0.894	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	46.5 0.415	51.3 0.459	74.8 0.668	76.3 0.682	78.1 0.698	76.7 0.686	56.6(18°) 0.598
Methyl alcohol, CH <sub>3</sub> . OH . . . . .	30	0.545	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	65 0.294	46 0.251	53.5 0.292	52 0.284	56 0.305	61 0.332	60 0.327
Ethyl alcohol, C <sub>2</sub> H <sub>5</sub> . OH . . . . .	24	1.087	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	29.2 0.295	21.9 0.238	24.6 0.267	21.4 0.232	22.5 0.244	26.3 0.285	26 0.28
Acetone, CH <sub>3</sub> . CO. CH <sub>3</sub> . . . . .	21	0.3158	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	102.8 0.294	68.6 0.217	69.7 0.220	105.0 0.332	117 0.370	115.9 0.366	128 0.40
Furfural, C <sub>4</sub> H <sub>3</sub> O. CHO . . . . .	41	1.494	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	19.6 0.293	12.7 0.190	14.4 0.215	— —	— —	28.4 0.424	— —
Acetonitrile, CH <sub>3</sub> . CN . . . . .	35	0.346	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	85 0.294	81 0.28	89 0.31	— —	100 0.35	109 0.38	126 0.44
Epichlorhydrin, ClCH <sub>2</sub> . C <sub>2</sub> H <sub>5</sub> O . . . . .	22	1.03	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	28.6 0.295	— 0.338	— —	31.8 0.328	35.2 0.363	35.4 0.365	— —
Pyridine, C <sub>5</sub> H <sub>5</sub> N . . . . .	12	0.890	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	35 0.294	25 0.22	30 0.27	— —	— —	47 0.42	50 0.45

TABLE II.—IONIC MOBILITIES AT 25° C.

Solvent.	H <sup>+</sup> .	Li <sup>+</sup> .	Ag <sup>+</sup> .	NH <sub>4</sub> <sup>+</sup> .	H <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> <sup>+</sup> .	H <sub>2</sub> N(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> <sup>+</sup> .	NO <sub>2</sub> <sup>-</sup> .	C.O. <sub>4</sub> <sup>-</sup> .	Picrate <sup>-</sup> .
Water . . . . .	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	38.9 0.347	53.9 (18°) 0.569	74.3 0.664	38 0.34	38 0.34	71 0.634	58.4 0.616	30.1 0.269
Methyl alcohol . . . . .	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	143 0.213	3.14 0.284	59 0.322	56 0.305	47 0.256	61 0.832	69 0.376	49 0.267
Ethyl alcohol . . . . .	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	17.6 0.192	17 0.185	22 0.24	25.7 0.279	20.9 0.227	26 0.282	— —	24.2 0.263
Acetone . . . . .	$\left\{ \begin{array}{l} l \\ l \times \eta \end{array} \right.$	70.8 0.224	— —	88 0.278	91.4 0.289	92.4 0.292	— —	115.6 0.365	84.2 0.266

expect from the sizes of the atoms. In addition to the five non-aqueous solvents of Tables I. and II. this is qualitatively observed in formamide, glycerol, ammonia, and selenium oxychloride. (In acetone, the positive ions Li, Na, K migrate with almost the same velocity; Li seems to be faster than the two others, but the fact is not quite certain.)<sup>5</sup> In the halogen series the sequence differs from that in water, the value being  $l_{I^-} > l_{Br^-} > l_{Cl^-}$ , just as in the alkalis.<sup>6</sup> (Further examples in the *Fort.*, p. 53.)

3. The ratio of the mobilities of small ions (presumably solvated) to those of large ions (not admitting of solvation) is throughout much smaller than it is in water, and it is subject to strong fluctuations (Table III., columns 2 and 3).

4. Equally remarkable fluctuations are observed in the ratios of the mobilities of inorganic anions and of cations (Table III., columns 4 and 5). The mobilities of these ions are of very similar magnitude in water and in the alcohols, but in acetone, furfural, and pyridine, the halogen-ions migrate  $1\frac{1}{2}$  and 2 times as fast as the alkali-ions; acetonitrile occupies an intermediate position.

TABLE III.  
RATIOS OF IONIC MOBILITIES.

Solvent.	$l_{Na^+}/l_{N(C_2H_5)_4^+}$	$l_{Cl^-}/l_{picrate^-}$	$l_{Cl^-}/l_{Na^+}$	$l_{I^-}/l_{K^+}$
Water { 25° . . .	1.555	2.54	1.49	1.027
{ 100° . . .	1.485 <sup>7</sup>	2.20 <sup>7</sup>	1.36 <sup>7</sup>	1.1 (estimate)
Methyl alcohol . . .	0.85	1.06	1.13	1.14
Ethyl alcohol . . .	0.81	0.88	0.98	1.07
Acetone . . .	0.74	1.25 (estimate)	1.53	1.65
Acetonitrile . . .	0.95	—	1.18	1.22
Furfural . . .	0.65	—	—	1.97
Pyridine . . .	0.76	—	—	1.57

In the discussion of these results we start from two suppositions which may be regarded as sufficiently established by this time: (1) there is a *stable solvation*, i.e., well-adhering water envelopes are formed; (2) Stokes' law of hydrodynamic friction holds also for small ions in general in sufficient approximation, so that the radii calculated on its basis from the mobilities come at least pretty near the actual radii of the migrating (eventually solvated) ions. These suppositions are based upon the arguments of Debye<sup>8</sup> and of Schmick;<sup>9</sup> the latter revised, on the instigation of Born, the hypothesis of Born of 1920 negating the stable solvation and the applicability of hydrodynamic laws to small ions. The validity of Stokes' law is moreover confirmed by numerous and manifold experimental data. Decided exceptions have only been observed in aqueous solutions, and this only for a certain group of ions; these exceptions are of a very

<sup>5</sup> See Walden, Ulich, and Busch, *l.c.*, p. 469.

<sup>6</sup> Matters are in acetone and ammonia as in water ( $l_{Br^-} > l_{I^-} > l_{Cl^-}$ ); sulphur dioxide follows the majority.

<sup>7</sup> In the case of  $l_{Na^+}/l_{N(C_2H_5)_4^+}$  the ratio 1.485 seems to mark a limiting value which remains constant with rising temperature. The ratios 2.20 and 1.36 for  $l_{Cl^-}/l_{picrate^-}$ , and  $l_{Cl^-}/l_{Na^+}$  are, however, not yet to be regarded as limits. The ratios in the other solvents are most probably constant for different temperatures.

<sup>8</sup> Marx, *Handbuch der Radiologie*, Vol. VI.

<sup>9</sup> Schmick, *Z. f. Physik*, 1924, 24, 56.

'complex and so far unexplained character.<sup>10</sup> The two suppositions supply a basis for calculating the radii of the migrating ions and, by their comparison with the radius of the ionic body proper, the degree of solvation. Stokes' law applied to ionic migration gives the following relation between the radius  $r$  (in cm.) of the ion and the product  $l\eta$  ( $l$  in Kohlrausch units,  $\eta$  in absolute units):  $r = 8.15 \cdot 10^{-9}/l\eta$ .

The radius  $r_0$  of the ion proper is not the radius of the external electronic shell, but the radius of the space occupied (sphere of influence of R. Lorenz). We purposely allow considerable latitude for this quantity which cannot be defined exactly; we accept broadly the value deduced from lattice girder measurements.<sup>11</sup> Deducting then the mol. volume of the ion body proper ( $N \cdot \frac{4}{3}\pi r_0^3$ ) from the ionic volume ( $N \cdot \frac{4}{3}\pi r^3$ ) calculated by Stokes' law, we obtain the space  $V_s$ , occupied by the solvation envelope. We should naturally find too small a value for the solvation number (molecules bound per ion), if we divided this  $V_s$  by the mol volume of the pure solvent, since owing to the strong ionic forces the packing of the molecules in the envelope will be much denser than in the free solvent. As we have, apart from water, to deal exclusively with organic solvents, we shall scarcely obtain too low a value for the solvation number, if we divide the  $V_s$  by the experimentally-determined true molecular volumes of organic (not hydrated) kations of R. Lorenz.<sup>12</sup> We thus find for each  $V_s$  the mean number of atoms of those organic molecules, the true mol. volume (not including any inter-molecular spaces) of which is just equal to this  $V_s$ ; we presume that we thereby determine likewise the number of the atoms within the envelope of an ion. When we then divide this number by the number of atoms in a molecule of the solvent, we shall have arrived at the solvation number.<sup>13</sup>

TABLE IV.  
SOLVATION NUMBERS.

Solvent.	Li <sup>+</sup> .	Na <sup>+</sup> .	K <sup>+</sup> .	Cl <sup>-</sup> .	Br <sup>-</sup> .	I <sup>-</sup> .
Water . . . .	6.7	2.4	—	—	—	—
Methyl alcohol . . . .	7	5.6	4	4	2.4	0.3
Ethyl alcohol . . . .	6	4.5	3.4	4.5	4	2.3
Acetone . . . .	4	4.5	4	2	1	0.1
Acetonitrile . . . .	—	5	3.4	—	1.3	0.2
Furfural . . . .	—	5	4	—	—	0.1
Pyridine . . . .	—	4	2.3	—	—	0.1

Some of the solvation numbers deduced in this way are given in Table IV. It will be seen that the envelope thickness is as a rule probably not of more than one molecule. The solvation of the kations appears to be fairly constant for all solvents, whilst that of the anions is decidedly smaller in acetone, furfural, and pyridine than in the alcohols. The iodine-ion seems practically to have no fixed envelope in these solvents, as also in others, not tabulated. This small solvation value of the anions might explain

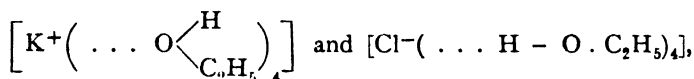
<sup>10</sup> Details in *Fort.*, p. 41.

<sup>11</sup> We adopt the following values for  $r_0$ ,  $10^8$  in cm.: Li + 0.5 to 1.5; Na + 0.8 to 1.5; K + 1.0 to 2.0; Cl - 1.0 to 2.0; Br - 1.2 to 2.2; I - 1.5 to 2.5.

<sup>12</sup> R. Lorenz, *Raumerfüllung und Ionenbeweglichkeit*. Leipzig, 1922, p. 80.

<sup>13</sup> We obtain approximately the same figures when we assume the mol. volume of the solvent in the envelope to be equal to the true mol. volume, and ascribe to the latter, on the strength of kinetic considerations, from  $\frac{1}{3}$  to  $\frac{1}{2}$  of the observed value.

the striking values of the transference numbers in the same solvents (Table III.). The cause of this peculiarity lies, we may feel certain, in the molecular structure of this solvation layer; it seems to be a case of molecules consisting of pronouncedly electronegative atoms (O, N) and further only of hydrocarbons, whilst the alcohols and water are characterised by the further presence of a positive H-atom (in the OH-group). We may plausibly assume that this H-atom induces the greater solvation also of the anions in these media, whilst the molecules of the other type can only react with the kations under the influence of forces of sufficient intensity. An essential factor in these effects is the degree of spatial approach which the molecular structure permits to the pole of the solvent molecule attracted by the ion. It seems obvious that the positive end of the dipole of acetone, furfural or pyridine, assumed to exist in the hydrocarbon core, will be less able to approach an attracting ion and will, moreover, claim more space in its approach than the negative end of this molecule or one of the poles of the OH-dipole. In the symbols of the chemistry of complexes, such solvates should then be represented in the following way: in ethyl alcohol:



in acetone  $[K^+(O = C(CH_3)_2)_4]$  and  $[Cl^-(\dots (C_3H_6) = O)_2]$ .

Another factor to be considered in the solvation problem is the nature of the ion. In addition to the much discussed influences of the magnitude of the charge and the diameter of the ion we have, in ions of complex structure, to pay attention to the seat of the charge. We can then understand why organic anions (carbo-, sulpho-, arseno-acids) as a rule betray solvation by an inconstancy of the  $\eta$ -product and a slow velocity of migration.<sup>14</sup> They are really oxygen-ions with some attachment which more or less impairs, according to its shape, the solvation of this O<sup>-</sup>ion; this is shown in a perfect manner by the picric and styphnic acids, and less markedly in the substituted benzoic and acetic acid. (For particulars see *Fort.*, pp. 39 and 52.)

Whilst the relations between ionic mobilities and ionic properties generally have attracted frequent attention, the relations between the ionic mobility and the molecular structure of the solvents (which can experimentally be studied by the new method of determining the mobilities), can claim particular interest at the present when Debye's fundamental researches have rendered a serious advance in the exploration of the dipole properties of molecules possible.

## THE MOBILITIES OF THE ELEMENTARY IONS IN METHYL ALCOHOL.

By H. HARTLEY and H. R. RAIKES.

*Received 30th March, 1927.*

The mobilities of the elementary ions possess a special interest as their structure is known more definitely than that of composite ions such as NO<sub>3</sub><sup>-</sup>, and some evidence as to their relative sizes may be obtained from

<sup>14</sup> R. Lorenz, *loc. cit.*, pp. 87 and 261.

their effective ionic radii in the crystal lattice which have been shown to be approximately constant in simple polar assemblages. In water, as is well known, the ions of the alkali metals and of the halogens, which have the largest radii in the crystal lattice, have the highest mobilities, while all the ions of the divalent metals have roughly the same mobilities in spite of a considerable increase in size with atomic number. These facts are usually explained by the assumption that the ions are hydrated, and that the degree of hydration of the small ions is larger on account of the more intense electrical field around them, their mobilities being correspondingly reduced. Washburn's determination of the relative number of water molecules associated with the ions of the alkali metals affords strong evidence in favour of this view.

We have been engaged since 1921 in investigating the conductivities of dilute salt solutions in methyl alcohol, and our results, together with the determination of the transport number of the chlorine ion in hydrogen chloride by Nonhebel and Hartley,<sup>1</sup> now enable us to compare the infinite dilution values of the mobilities of all the univalent elements and most of the divalent metals in methyl alcohol with those in water at 25° C.

The values in Table I. for univalent ions in methyl alcohol are taken from Frazer and Hartley's<sup>2</sup> paper, with the exception of Tl<sup>+</sup>, the rest are from unpublished work by McClhery (Tl<sup>+</sup>), Philbrick (Ca<sup>++</sup>, Sr<sup>++</sup>, Ba<sup>++</sup>), and Ross (Mg<sup>++</sup>, Zn<sup>++</sup>, Cd<sup>++</sup>).

TABLE I.  
IONIC MOBILITIES AT 25° C.

	H <sub>2</sub> O.	MeOH.		H <sub>2</sub> O.	MeOH.		H <sub>2</sub> O.	MeOH.
H .	349	142.2	F .	54.4	40.2	Mg .	53.0	57.6
Li .	39.6	39.6	Cl .	75.4	51.3	Ca .	59.8	60.0
Na .	50.9	45.7	Br .	77.5	55.5	Sr .	59.8	59.0
K .	74.4	53.8	I .	76.0	61.0	Ba .	64.2	60.0
Rb .	77.6	57.4	—	—	—	Zn .	54.2	59.6
Cs .	78.1	62.3	—	—	—	Cd .	53.8	57.4
Ag .	63.0	52.2	—	—	—	—	—	—
Tl .	75.9	60.6	—	—	—	—	—	—

In methyl alcohol as in water the mobilities both of the alkali metals and halogens increase with atomic number, the rise being more regular in methyl alcohol (in water for example the mobility of bromine is slightly greater than that of iodine). The mobilities of silver and thallium are high in both cases, and bear roughly the same relation to caesium in each. The mobilities of the divalent metals are even more nearly equal in methyl alcohol than in water. Thus the general relationships of the ionic mobilities are the same in both solvents, as is seen in the figure, in which the mobilities of the ions divided by their valencies are plotted against their atomic numbers. This expresses the relative magnitudes of their mobilities under equivalent conditions, as in the same electrical field the force acting on a divalent ion is twice that on a univalent ion.

In spite, however, of the general agreement the relative mobility of the ions in the two solvents is not constant, as is seen in Table II. for univalent ions. Values for the divalent ions are all approximately unity like lithium.

If the change in mobility were due entirely to the change in the viscosity of the solvent, the ratios in Table II., would all have the value 1.64, the ions

TABLE II.

	Li.	Na.	K.	Rb.	Ca.	Ag.	Tl.	F.	Cl.	Br.	I.
$\frac{\mu_{\text{MeOH}}}{\mu_{\text{H}_2\text{O}}}$	1	0.90	0.72	0.74	0.80	0.83	0.80	0.74	0.68	0.71	0.81

moving faster in the less viscous solvent. But some other factor is concerned which varies from ion to ion; if it is solvation then the above ratios indicate that the ions are more solvated in methyl alcohol than in water.

It is hard to gain more precise information about solvation in methyl alcohol as experiments similar to Washburn's would be very difficult owing to the volatile and hygroscopic nature of the solvent and to the limited solubility of substances in it. Schmick's work,<sup>8</sup> however, makes it probable that the electric field around the smaller ions is sufficiently strong to hold firmly the dipole molecules in their immediate vicinity. This accords with

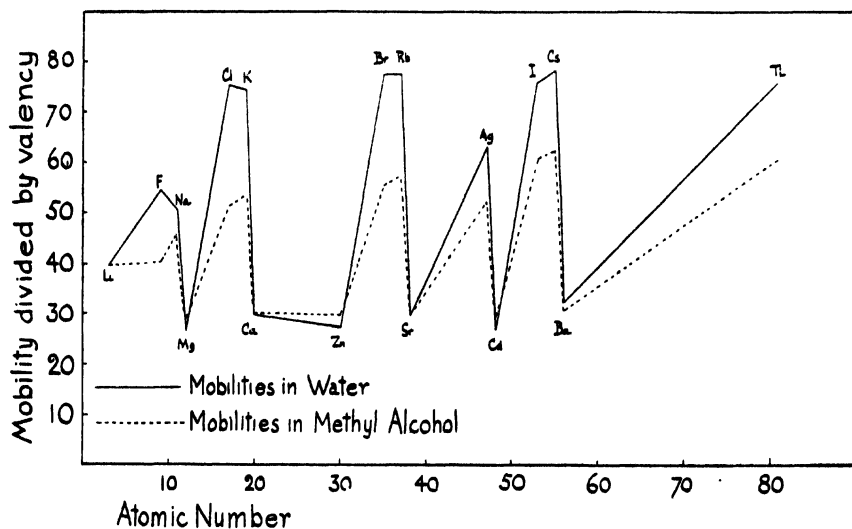


FIG. 1.

the general trend of recent experimental work in non-aqueous solvents, which indicates that Stokes' Law is applicable to the motion of ions,<sup>4</sup> and that the ionic radii calculated by means of it give at any rate the relative magnitudes of the ions in different solvents. Table III. gives a comparison

TABLE III.  
IONIC RADII IN ÅNGSTROM UNITS.

	Water.	Methyl Alcohol.	Crystal Lattice.		Water.	Methyl Alcohol.	Crystal Lattice.		Water.	Methyl Alcohol.	Crystal Lattice.
Li	2.30	3.78	0.72	F	1.67	3.72	1.33	Mg	3.44	5.19	0.75
Na	1.79	3.27	1.01	Cl	1.21	2.91	1.72	Ca	3.05	4.98	1.02
K	1.22	2.78	1.30	Br	1.18	2.69	1.92	Sr	3.04	5.06	1.20
Rb	1.17	2.60	1.50	I	1.20	2.45	2.19	Ba	2.83	4.93	1.40
Cs	1.17	2.40	1.75	—	—	—	—	Zn	3.36	5.02	(0.60)
Ag	1.44	2.86	(1.03)	—	—	—	—	Cd	3.38	5.21	(0.98)
Tl	1.20	2.47	(1.53)	—	—	—	—	—	—	—	—

of the ionic radii in water and methyl alcohol calculated from their mobilities by means of Stokes' Law, together with their effective ionic radii in the crystal lattice as calculated by Wasastjerna,<sup>5</sup> with the exception of the values in brackets which were obtained by subtracting 0.72 from the values given by Bragg.<sup>6</sup>

The fact that the ionic radii in water of several of the alkali metals and halogens appear to be smaller than their effective radii in the lattice throws some doubt on the absolute values of the radii obtained by these means.

The radii of all ions in methyl alcohol are greater than in water, the increase in apparent size being due presumably either to the larger solvent molecules or the greater number attached to the ion, the increase being greater for the univalent than the divalent ions. The influence of the ionic charge on the degree of solvation is shown by the fact that in both solvents all the divalent ions have the largest radii, although the radii in the crystal lattice vary from 0.75 Ångströms for magnesium to 1.40 for barium, the greater degree of solvation of the smaller ion just compensating for the increased size of the ions of higher atomic number. The effect of size appears again clearly among the univalent ions, where the order of magnitude is the inverse of that for the crystal lattice. Silver which is smaller than rubidium and caesium in the lattice has a smaller mobility in both solvents, while thallium which is larger in the lattice is also faster, having roughly the same mobility as rubidium and caesium. It is worth mentioning in this connection that the mobility of the perchlorate ion in methyl alcohol is 70.8 as compared with 51.3 for chlorine.

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- <sup>2</sup> Frazer and Hartley, *Proc. Roy. Soc.* (1925), 109A, 351.
- <sup>3</sup> Schmick, *Z. Physik.* (1924), 24, 56.
- <sup>4</sup> Ulich, *Über die Beweglichkeit der elektrolytischen Ionen*, Berlin, 1926.
- Walden, Ulich, and Busch, *Z. physikal. Chem.* (1926), 123, 429.
- <sup>5</sup> Wasastjerna, *Soc. Scient. Fenn. Comm. Phys. Math.* (1923), 38, 1.
- <sup>6</sup> Bragg, *Phil. Mag.* (1926), (7), 2, 258.

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## NOTES ON THE DEBYE-HÜCKEL THEORY.

BY H. HARTLEY AND R. P. BELL.

*Received 9th April, 1927.*

The Debye-Hückel theory of the conductivity of strong electrolytes postulates that the decrease in ionic mobility with increasing concentration is due entirely to interionic forces and to cataphoresis of the solvent, the electrolyte being completely dissociated at all concentrations at which the theory is applicable. In water it is probable that this latter condition is fulfilled for most salts in dilute solution, although certain salts of mercury and cadmium are exceptions; but in non-aqueous solvents the formation of complex ions or of undissociated molecules even in dilute solutions is a much more general phenomenon. Thus

discrepancies between the Debye-Hückel theory and experimental results may mean either that the theory is incorrect, or that the electrolytes in question are not completely dissociated. It is therefore a matter of great interest to see whether there is a substantial body of evidence in accord with the theory. If this is so, deviations from the theory might be ascribed to abnormal behaviour of the electrolyte and might even be used to detect lack of complete dissociation.

Debye and Hückel have made a comprehensive survey of the conductivity data for dilute aqueous solutions, and have shown that they are in fair agreement with their theory. Similar comparisons for non-aqueous solvents are more difficult, as the experimental data are far less complete and homogeneous, but as such a comparison affords a more searching test of this general applicability of the theory in view of the large differences in properties between the solvents, we have examined a considerable number of the conductivity data for dilute salt solutions in thirteen different solvents, in order to see how far they are in agreement with the theory. Owing to the absence of reliable data for polyvalent ions the comparison is limited to uni-univalent salts. For electrolytes of this type Debye and Hückel's equation can be written in the form,

$$\frac{\Lambda_0 - \Lambda_c}{\Lambda_0} = \left( \frac{K_1}{D^{3/2}} w_1 + \frac{K_2}{D^{3/2}} b \right) \sqrt{2c} \quad . \quad . \quad . \quad (1)$$

where  $K_1$  and  $K_2$  are universal constants for all solvents varying only with the temperature,  $D$  is the dielectric constant of the solvent,

$$w_1 = \frac{1}{2} \left( \frac{l_a}{l_c} + \frac{l_c}{l_a} \right)$$

$l_c$  and  $l_a$  being the mobilities of the cation and anion,  $b$  is the harmonic mean of the ionic radii and  $C$  is the molecular concentration.

Obviously the first test of this equation is to see whether there is in all cases a linear relation between the equivalent conductivity and the square root of the concentration, corresponding to the empirical expression found by Kohlrausch to hold for dilute aqueous solutions:—

$$\Lambda_c = \Lambda_0 - \kappa c^{1/2} \quad . \quad . \quad . \quad . \quad (2)$$

Hartley and Frazer have shown that this relation does hold for eighteen uni-univalent salts in methyl alcohol up to 0.002  $N$ , and subsequent work has confirmed this for a large number of other salts. Walden, Ulich, and Busch have found the same relation for salts in acetone up to 0.0005  $N$ , while Ulich has recently used the square root formula in recalculating values of  $\Lambda_0$  in a number of solvents. We have examined a large number of experimental results in the thirteen non-aqueous solvents mentioned in Table I. by graphic methods, and we find that in general the more accurate and concordant are the data, the more closely do they confirm to the square root relation in dilute solution. In view of the wide range of solvents and the number of salts examined, it is a remarkable fact that the square root law was found to hold so generally.

The dilution at which the linear relationship ceases varies with the solvent, the solute and the temperature. It is interesting to note that in some non-aqueous solvents certain lithium salts do not obey this relation or do so only at exceptionally high dilutions; lithium iodide, however, shows no such abnormality, and there is little doubt that the exceptional behaviour of lithium salts is due to the formation of complex

ions even in dilute solutions, as in non-aqueous solvents the tendency to form complexes appear to be less with the iodine ion than with the other halogens or the nitrate ion.

Comparatively little work has been done on conductivity in non-aqueous solvents over a wide range of temperature, but the measurements of Duperthuis in pyridine and various alcohols between 0° C. and 80° C. indicate that the range of applicability of the square root relation is diminished at higher temperatures. However, it must be remembered that the difficulties in the way of accurate conductivity measurements in dilute solution are greatly increased when the temperature exceeds 25° C.

Since it seems clear that the square root relation is obeyed at high dilutions within the limits of experimental error, except where there is reason to suspect the absence of complete dissociation, it is possible to apply a further test to the theory by considering the slope of the conductivity-concentration curve. This depends *inter alia* on "*b*," the harmonic mean of the ionic radii, and by combining equations (1) and (2) we have for a uni-univalent electrolyte,

$$b = \left( \frac{x}{\sqrt{2}\Lambda_0} - \frac{K_1}{D^{1/2}w_1} \right) \frac{D^{1/2}}{K_2} \quad (3)$$

It is therefore possible to calculate values for *b* if  $\Lambda_0$ , *x*,  $K_1$ ,  $K_2$ , *D* and  $w_1$  are known.

But Debye and Hückel assume that at infinite dilution the motion of the ions obeys Stokes' law, and therefore the radius of the ion *r* can be calculated from the equation,

$$\text{Velocity} = \frac{\text{Force}}{6\pi\eta r} \quad (4)$$

where  $\eta$  is the viscosity of the solvent

If  $l_o$  is the mobility of the ion at infinite dilution, equation (4) becomes

$$l_o = \frac{8.15 \times 10^{-9}}{\eta \times r},$$

or considering the sum of the mobilities

$$\Lambda_0 = \frac{8.15 \times 10^{-9}}{\eta} \left( \frac{1}{r_a} + \frac{1}{r_c} \right)$$

so that from the known values of  $\Lambda_0$  and  $\eta$ , values of the harmonic mean of the ionic radii can be calculated and compared with the values of *b* obtained from the slope of the conductivity curve.

The results of such calculations for potassium, sodium, and tetraethyl-ammonium iodides in fourteen solvents are given in Table I. Owing to lack of knowledge of the transport numbers in propyl, isobutyl, and isoamyl alcohol, in acetophenone, sulphur dioxide and ammonia, some uncertainty attaches to the values of *b* in these solvents. The transport number has been assumed to be 0.5; if the ions moved with unequal speeds the effect would be to reduce the value of *b* (Debye), but in isobutyl alcohol for example, even if one ion had three times the mobility of the other, the value of *b* for sodium iodide would only be reduced from 13.0 to 10.0.

In Table I. the solvents are arranged in the order of their dielectric constants, which are given in column 1; column 2 gives their viscosities

Solvent.	D.	$\eta$ .	Potassium Iodide				Sodium Iodide.				Tetraethylammonium Iodide.			
			$\Lambda \circ$ .	$z$ .	$b \times 10^8$ Debye.	$b \times 10^8$ Stokes.	$\Lambda \circ$ .	$z$ .	$b \times 10^8$ Debye.	$b \times 10^8$ Stokes.	$\Lambda \circ$ .	$z$ .	$b \times 10^8$ Debye.	$b \times 10^8$ Stokes.
Water . . . . .	81	0.00893	130.5 (f)	72.7	0.50	1.19	—	—	—	—	110.3 (m)	153	2.10	1.65
Acetonitrile . . . . .	35	0.00351	199.0 (o)	685	6.75	2.34	190.8 (a)	636	6.57	2.44	193.7 (o)	446	1.60	2.40
Methyl alcohol . . . . .	30	0.00545	114.9 (c)	260	1.19	2.55	{ 42.8 (bb)	178	3.69	3.07	118.1 (o)	297	1.69	2.48
Ethyl alcohol . . . . .	26	0.0109	45.1 (bb)	177	3.26	2.92	{ 44.5 (a)	174	3.69	3.07	52.2 (m)	223	3.88	2.87
" " " " " "	26	—	—	—	—	—	{ 51.6 (k)	202	6.30	2.53	—	—	—	—
Benzonitrile . . . . .	26	0.0125	—	—	—	—	{ 21.3 (l)	117	4.67	3.30	53.5 (o)	263	4.95	2.44
Propyl alcohol . . . . .	22	0.0322	—	—	—	—	{ 22.5 (g)	117	4.19	3.27	—	—	—	—
" " " " " "	22	—	—	—	—	—	311.5 (g)	1970	3.46	2.05	—	—	—	—
Ammonia " " " " " "	22	0.00256	350.0 (g)	1730	1.48	1.84	{ 172.5 (b)	907	4.22	2.86	209.0 (p)	1300	6.55	2.47
Acetone . . . . .	21	0.00316	{ 174.0 (b)	925	4.65	2.84	{ 178.0 (a)	1070	5.56	2.84	—	—	—	—
" " " " " "	21	—	{ 185.6 (p)	977	4.46	2.78	{ 184.5 (p)	980	4.34	2.80	—	—	—	—
" " " " " "	21	—	—	—	—	—	{ 12.5 (d)	150	13.0	3.34	—	—	—	—
Isobutyl alcohol . . . . .	19	0.0332	—	—	—	—	{ 13.5 (d)	200	17.2	3.64	—	—	—	—
" " " " " "	19	—	—	—	—	—	{ 146.0 (k)	1230	6.78	2.78	151.0 (m)	1450	8.73	2.69
Methyl ethyl ketone . . . . .	18	0.00402	109.0 (m)	590	0.97	3.72	{ 9.4 (d)	208	24.6	4.60	—	—	—	—
Isoamyl alcohol . . . . .	16	0.0377	9.7 (d)	268	31.0	4.45	{ 11.72 (h)	295	28.6	3.70	—	—	—	—
" " " " " "	16	—	—	—	—	—	{ 40.9 (t)	396	7.17	2.21	—	—	—	—
Acetophenone . . . . .	15.5	0.0180	—	—	—	—	—	—	—	—	—	—	—	—
Sulphur dioxide . . . . .	13.6	0.00452	218.5 (e)	3800	12.6	1.65	{ 62.6 (l)	585	4.47	2.62	—	—	—	—
Pyridine . . . . .	12.3	0.00958	66.5 (f)	1180	14.5	2.48	{ 60.4 (a)	575	4.67	2.82	—	—	—	—
" " " " " "	12.3	—	{ 70.6 (a)	1280	15.8	2.42	—	—	—	—	—	—	—	—

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at 25° or at the highest temperature for which conductivity data are given. Under the heading of each salt the first column gives the value of  $\Lambda_0$  at the temperature shown in the reference to the author at the foot of the table, the second column the value of  $x$  in equation (2), the third column the value of  $b$  calculated from the slope of the curve, the fourth column the value of  $b$  calculated by Stokes' law. In some cases values are given for the same salt obtained by different observers in order to show the degree of concordance of independent determinations.

The results in the table do not show any well-marked regularity, though it is clear that the values of  $b$  calculated from Stokes' law rarely differ from one another by more than a factor of two, while the values from Debye's equation show much larger variations, and in general show greater divergencies from the Stokes' values in solvents of low dielectric constant, although there are apparent exceptions to this in ammonia, methyl ethyl ketone, and for sodium iodide in pyridine. The contrast between the iodides of sodium and potassium in this solvent is curious. Likewise the difference between the behaviour of tetraethylammonium iodide and the two alkali metal iodides in acetonitrile. The table certainly emphasises the need for further experimental work to confirm such differences and to make the data more complete.

The rough correspondence between the two sets of values for  $b$  in all solvents with a dielectric constant greater than 20 is evidence of the essential correctness of Debye and Hückel's theory. In view of the two methods of calculation it is perhaps remarkable that they agree so well. The abnormally large values of  $b$  found in the higher alcohols, for instance, shows that conformity to the square root relation is no guarantee that the variation of the conductivity with concentration will be in accordance with Debye's equation. The same point emerges from Walden, Ulich and Busch's work in acetone, where in spite of the validity of the square root relation, the slopes of the curves vary to a much greater extent than could be accounted for by Debye's theory, and indicate probably lack of complete ionization.

## THE IONISATION OF SOME TYPICAL STRONG ELECTROLYTES.\*

By DUNCAN A. MACINNES and IRVING A. COWPERTHWAIT.

*Received 5th March, 1927.*

If the theory of complete dissociation of aqueous solutions of strong electrolytes is true, it would seem probable that the properties of these solutions would be additive in nature at much higher concentrations than if the facts are represented by the Arrhenius theory. According to the theory of complete dissociation it would, for instance, be expected that the conductance contributed to a 0.1 *N* solution by the chloride ion would be nearly if not exactly the same whether the ion is associated with hydrogen or potassium ions, since the chloride ion concentration is, according to this theory, the same in these two solutions. The Arrhenius theory, on the other hand,

\* Contribution from the Research Laboratory of Physical Chemists, Massachusetts Institute of Technology, No. 197, and from the Laboratories of the Rockefeller Institute for Medical Research.

calls for quite different degrees of dissociation for hydrochloric acid and potassium chloride solutions (92.5 per cent. and 86.0 per cent., respectively). According to this latter theory therefore the contribution of the chloride ion to the conductance of the solution would be different since the chloride ion concentrations are different. Now the conductance arising from the presence of chloride ion in these solutions is equal to the product  $T_{Cl}\Lambda$  in which  $T_{Cl}$  is the transference number of the chloride ion and  $\Lambda$  is the equivalent conductance. It is therefore quite evident that accurate transference numbers are of interest in deciding between the two theories. By means of a modification of Denison and Steele's<sup>1</sup> moving boundary method for determining transference numbers MacInnes and Smith<sup>2</sup> have made accurate determinations of the transference numbers at 25° of three chlorides at 0.1 *N*, and a determination of the value for  $NH_4Cl$  has been carried out by the same method by T. C. Huang.<sup>3</sup> The transference numbers and the corresponding  $T_{Cl}\Lambda$  products for the chloride ion are given in Table I. It

TABLE I.  
CONDUCTANCES OF THE CHLORIDE ION FROM 0.1 *N* SOLUTIONS OF DIFFERENT CHLORIDES AT 25° C.

So'n.	Equiv. Cond. $\Lambda$	Trans. No. $T_{Cl}$	$T_{Cl}\Lambda$
HCl . . .	390.4	0.1680	65.59
KCl . . .	129.0	0.5080	65.53
NaCl . . .	106.8	0.6137	65.54
$NH_4Cl$ . . .	128.55	0.5100	65.56

will be seen in column four that this product is the same, well within the limit of experimental error.<sup>4</sup> Thus the chloride ion contributes the same amount to the equivalent conductivity in all these solutions. The figures given in Table I. prove that these chlorides have the same degree of dissociation. They do not, however, prove that the dissociation is complete. That these substances are substantially completely dissociated appears highly probable from the fact that no properties, differing from those of the ions, have so far been assigned to the undissociated portion of strong electrolytes, although the theory of Arrhenius calls for the presence of considerable amounts of electrolyte not in the form of ions. Further, the remarkable success of the Debye-Huckel theory is also strong evidence in favour of complete dissociation.

So far as the small amount of accurate data at present available enables us to decide, the alkali halides and the halogen acids all show an additivity of the conductance of their solutions, at any one concentration, similar to that shown in Table I.<sup>5</sup> There is, however, a group of strong electrolytes which do not show this additivity. This group includes certain of the nitrates, chlorates, and iodates. Although no accurate transference data have been published for these substances, their exceptional nature can be

<sup>1</sup> Denison and Steele, *Phil. Trans. (A)* **205**, 449 (1906); *Z. physik. Chem.*, **57**, 110 (1906-07).

<sup>2</sup> MacInnes and Smith, *J. Amer. Chem. Soc.*, **45**, 2246 (1923); **47**, 1009 (1925).

<sup>3</sup> Huang, not yet published.

<sup>4</sup> This constancy was pointed out by Lewis, *J. Amer. Chem. Soc.*, **34**, 1631 (1912), and more generally by MacInnes, *ibid.*, **43**, 1217 (1921), on the basis of the published transference and conductance data.

<sup>5</sup> See MacInnes, *J. Amer. Chem. Soc.*, **43**, 1217 (1921) for a partial summary.

demonstrated by an indirect method which we will not however discuss further here. As it has appeared that a study of these substances will throw light on some of the problems of electrolytic dissociation, we have begun an examination of the properties of these solutions. Since our measurements have, so far, been confined to a series of the nitrates at 0.1 *N*, this paper may be considered as a report of progress. The study has consisted in the determination of transference numbers and conductances of nitrates and of related substances when these were necessary for the interpretation of the data. A more complete account of these measurements will be published later.

Somewhat to our surprise we found evidence that, if the chlorides just discussed are completely dissociated, nitric acid and ammonium nitrate must have that degree of dissociation also. The evidence is given in Tables II. and III. It will be observed from the fourth column in each table that the

TABLE II.

THE CONDUCTANCE OF THE HYDROGEN ION FROM 0.1 *N* SOLUTIONS OF HYDROCHLORIC AND NITRIC ACIDS, AT 25° C.

Substance.	Equivalent Conductance, $\Lambda$ .	Trans. No. $T_{H^+}$	$T_{H^+} \Lambda$ .
$HNO_3$ . .	385.0	0.8441	325.0
$HCl$ . .	390.4	0.8320	324.8

TABLE III.

THE CONDUCTANCE OF THE AMMONIUM ION FROM 0.1 *N* SOLUTIONS OF AMMONIUM CHLORIDE AND NITRATE AT 25° C.

Substance.	Equivalent Conductance, $\Lambda$ .	Trans. No. $T_{NH_4}$	$T_{NH_4} \Lambda$ .
$NH_4NO_3$ .	123.0	0.5130	63.1
$NH_4Cl$ . .	128.6	0.4900	63.0

product of the equivalent conductance and the transference number is the same for the hydrogen and ammonium ions whether they are associated with nitrate or chloride ions. In the case of the hydrogen ion the agreement is within 0.07 per cent. The slightly greater deviation in the case of the ammonium salts may be due to the greater difficulty, due to hydrolysis, in the determination of the transference numbers of these compounds.

The other nitrates we have studied cannot, however, be considered to be completely dissociated, since the  $T_{NO_3} \Lambda$  products of these substances are all smaller than those of nitric acid and ammonium nitrate. The conductance and transference data for these substances are given in Table IV., and the  $T_{NO_3} \Lambda$  product again in the fourth column. The fifth column contains the degree of dissociation obtained by dividing each  $T_{NO_3} \Lambda$  product by that of nitric acid, the latter, as we have indicated above, being completely dissociated. Strictly, each  $T \Lambda$  product should be divided by that of a

TABLE IV.

THE CONDUCTANCE OF THE NITRATE ION FROM 0.1 N SOLUTIONS OF DIFFERENT NITRATES, AT 25° C.

Substance.	Equivalent Conductance, $\Lambda$ .	Trans. No. $T_{NO_3}$ .	$T_{NO_3}\Lambda$ .	Degree of Dissociation.
HNO <sub>3</sub> . . . .	385.0	0.1559	60.0	—
NH <sub>4</sub> NO <sub>3</sub> . . . .	123.0	0.4870	59.9	—
NaNO <sub>3</sub> . . . .	101.26	0.5903	59.77	0.996
KNO <sub>3</sub> . . . .	120.38	0.4872	58.65	0.978
AgNO <sub>3</sub> . . . .	109.23	0.5315	58.05	0.967

completely dissociated substance at the same ion concentration and requires a series of approximations, though the difference is inappreciable in the present case.<sup>6</sup> The difference between nitric acid, and ammonium nitrate and the other nitrates, cannot be due to experimental error since all the transference numbers were checked either by a separate determination of the transference number of the positive ion, and the two numbers were found to add up very closely to 1.000, or else, as in the case of silver nitrate, both lithium and sodium nitrates were used as indicator solutions. The conductance measurements agreed with those of Kohlrausch or with other reliable data, within a small experimental error.

It is interesting to note that Bjerrum,<sup>7</sup> from an entirely different point of view, has come to the conclusion, based on an extension of the Debye-Huckel theory, that certain electrolytes, among them potassium nitrate and potassium and sodium iodates, cannot be completely dissociated. His argument, if we represent it correctly, is that a certain proportion of the ions will form pairs which will act osmotically as single molecules, if one or both of the ions has a radius smaller than a certain critical value. Under these conditions the ions will approach so near to each other that the attraction of a positive ion for a given negative ion for instance will, for short periods, be greater than the combined attractions of all the surrounding positive ions on the negative ion. According to this author it is necessary to assume very small or even negative values for the ion diameters in the Debye-Huckel equations, if correction is not made for this association. Mueller,<sup>8</sup> in a paper of which only an abstract has appeared, claims, however, that if correction is made for certain simplifying assumptions used by Debye and Huckle, the theory of the latter will account for small ions without assuming association. It is evident that our measurements favour Bjerrum's computations although the latter call for larger degrees of association than we have found by the method described in this paper. It also seems probable that our method is a more accurate and definite measure of this association than that proposed by Bjerrum.

<sup>6</sup> This question is discussed in a paper by MacInnes, *J. Amer. Chem. Soc.*, **48**, 2068 (1926), in which it is shown that the mass law holds for relatively strong acids throughout a wide concentration range if ionisation values are obtained substantially as described above, and activity coefficients are computed according to the Debye-Huckel theory. See also Sherrill and Noyes, *ibid.*, **48**, 1861 (1926), who independently arrived at the same conclusions.

<sup>7</sup> Bjerrum, *Kgl. Danske Videnskabernes Selskab.*, vii., 9, p. 2 (1926).

<sup>8</sup> Mueller, *Physical Review*, **29**, 216 (1927).

## Summary.

Evidence is given, from transference and conductance measurements, that if the alkali chlorides and hydrochloric acid are completely dissociated, then nitric acid and ammonium nitrate belong in this class also. Sodium, potassium, and silver nitrates, however, must be partially associated.

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## ON THE AGREEMENT WITH EXPERIMENT OF THE DILUTION FORMULA DEDUCED FROM THE DEBYE-HÜCKEL THEORY.

BY ALLAN FERGUSON AND ISRAEL VOGEL.

*Received 8th April, 1927.*

The writers of this note have for some time past been engaged in a test of various dilution equations and, as it happens, have paid considerable attention to an equation of the form

$$\Lambda = \Lambda_0 - BC^n \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $\Lambda$  is the equivalent conductivity at a concentration of  $C$  gram-equivalents per litre.<sup>1</sup>

As is well known, Kohlrausch<sup>2</sup> has proposed equations of this form—one with  $n$  equal to  $\frac{1}{2}$ , another with  $n$  equal to  $\frac{1}{4}$ . More recently Lorenz<sup>3</sup> and Walden<sup>4</sup> have suggested that the index  $n$  shall be put equal to 0.45, and now Debye and Hückel<sup>5</sup> provide a rational basis for the form of the equation and deduce for  $n$  the value  $\frac{1}{2}$ —a value, be it noted, *which is independent of the nature of the electrolyte under investigation.*

Another attempt to find a rational dilution equation is that due to Ostwald who finds that, as a deduction from the law of mass action

$$(Ca)^2 = KC(1 - a) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $a$  stands for  $\Lambda/\Lambda_0$ . This equation holds at ordinary concentrations for weak electrolytes, though attempts<sup>6</sup> have been made to put it forward as a general law for all electrolytes at high dilutions—attempts which we deal with at length elsewhere.<sup>7</sup> It therefore becomes of interest to see what relation, if any, holds between the Ostwald dilution equation and that proposed by Debye and Hückel. Are they mutually exclusive? And—what is of primary importance—do they give a picture of the march of the conductivity with changing dilution which is an accurate representation of the facts?

As it stands, the Ostwald dilution equation is at no stage of the dilution

<sup>1</sup> *Phil. Mag.*, 1925, 50, 971.

<sup>2</sup> *Wiss. Abh. Tech. Reichsanst.*, 1900, 3, 156. "Das Leitvermögen der Elektrolyte," p. 107 (1916).

<sup>3</sup> *Z. anorg. Chem.*, 1919, 108, 191.

<sup>4</sup> *Ibid.*, 1921, 115, 49.

<sup>5</sup> *Physik. Zeit.*, 1923, 24, 305.

<sup>6</sup> Washburn, *Trans. Amer. Chem. Soc.*, 1918, 40, 122 and 150.

<sup>7</sup> *Phil. Mag.* In the Press.

in formal agreement with equation (1). But let us write it in the more general form first proposed by Storch<sup>8</sup>

$$\left(C \frac{\Lambda}{\Lambda_0}\right)^m = KC \left(1 - \frac{\Lambda}{\Lambda_0}\right) \quad (3)$$

and we have, since the discussion is restricted to dilutions such that the so-called viscosity correction may be neglected

$$\Lambda = \Lambda_0 - \frac{\Lambda^m}{K\Lambda_0^{m-1}} C^{m-1} \quad (4)$$

At high dilutions  $\Lambda$  changes but slowly with  $C$ , and it will be sufficiently accurate to put the approximate value  $\Lambda_0$  in the small term in (4) leading to

$$\Lambda = \Lambda_0 - \frac{\Lambda_0}{K} C^{m-1} = \Lambda_0 - B_1 C^{m-1} \quad (5)$$

which is of the form of equation (1). We have elsewhere shown, in an attempt to test the validity of the Ostwald law, that the Storch formula (3) either in its simple form, in which  $m$  is supposed independent of the concentration, or in a more general form in which

$$m = a + bC$$

represents very accurately the behaviour of electrolytes of all classes (in aqueous solution) over a very wide range of concentration. Moreover the results show not the slightest sign of deviation from the formula at low concentrations. Hence for the validity of the Ostwald formula it is necessary that  $m$  should be equal to 2 in the simple Storch equation, or  $a$  should equal 2 in the more general form. As our results will show this does not hold generally since, weak electrolytes apart, the only substances for which we find  $m$  equal to 2 are hydrochloric and iodic acids. If a substance follows Ostwald's law, we see, at least at low concentrations, that the conductivity should be approximately a linear function of the concentration. Hence if equation (1) be accepted as giving at least the *form* of a dilution equation legitimate at low concentrations, we have several mutually exclusive possibilities:—

(i) The conductivity may be a linear function of the concentration (Ostwald; Washburn).

(ii) The conductivity may be a linear function of the square root of the concentration (Kohlrausch; Debye-Huckel).

(iii) The conductivity may be a linear function of some other power of the concentration (Lorenz; Walden); and finally

(iv) The conductivity may be a linear function of some power  $n$  of the concentration, where  $n$  varies from electrolyte to electrolyte.

The possibility last-named seems to us to represent most accurately *the facts of observation*; and the process which we now describe both tests the form of the dilution equation and establishes the value of  $n$  without in any way forcing the facts.

If we draw a smooth curve through the plotted-out values of  $\Lambda$  and  $C$ , using appropriate splines, then tabulating values of  $\Lambda$  taken from the curve corresponding to values of  $C$  chosen in any known arbitrary geometrical progression, we have

$$\begin{aligned} \Lambda &= \Lambda_0 - BC^n \\ \Lambda + \delta\Lambda &= \Lambda_0 - B(rC)^n \\ \therefore \log \delta\Lambda &= n \log C - \log B(1 - r^n) \end{aligned}$$

so that  $\log \delta\Lambda$  plotted against  $\log C$  gives a straight line if, and only if, equation (1) holds good. Moreover the slope of the straight line determines  $n$  unambiguously, and the remaining constants are then easily determined.<sup>9</sup>

It will be seen that this procedure both tests the form of the equation and, the form being that of equation (1), determines the value of  $n$  without forcing the constants. We lay stress on this, as it may be seen that, a value for  $n$ , of say 0.55 being thus determined, the rectilinear graph will show that a line having a slope of 0.50 is outside the limits of experimental error.  $n$  being thus determined the constant  $B$  may be worked out, and finally from every pair of values of  $\Lambda$  and  $C$  we may calculate a value of  $\Lambda_0$  from the equation

$$\Lambda_0 = \Lambda + BC^n$$

and the mean of these gives the most probable value of  $\Lambda_0$ . Table I. below shows some of the values thus obtained for electrolytes of different nature; it will be noticed that  $\Lambda_0$  varies remarkably little in the determination for any one electrolyte.

TABLE I.

Concn. $\times 10^{-4}$ .	18° $\Lambda_0$ .				0° $\Lambda_0$ .		25° $\Lambda_0$ .	
	KCl.	NaF.	Ca(NO <sub>3</sub> ) <sub>2</sub> .	MgSO <sub>4</sub> .	NaCl.	KCl.	KMnO <sub>4</sub> .	KCl.
1	130.02	90.08	114.02	113.78	—	—	—	—
2	130.07	90.08	114.01	113.77	—	—	—	—
5	130.08	90.08	114.08	113.68	66.72	81.51	136.84	152.28
10	130.04	90.07	114.04	113.79	66.69	81.51	136.85	152.24
20	130.00	90.08	113.96	—	66.67	81.48	136.82	152.30
50	130.00	90.09	113.96	—	66.64	81.41	136.77	152.26
100	130.07	90.11	114.10	—	66.85	81.51	136.82	152.23

We emphasise the technique of the method, as we desire to point out that *the straight line which determines  $n$  is drawn without any preconceptions concerning the value of  $n$* . It is perfectly true that, if the value of  $n$  so determined is near to 0.5, the assumption that the square root law is followed will give a fairly good fit by slight alterations in the constants  $\Lambda_0$  and  $B$ . On this account it is all the more misleading to adopt this procedure, as it hides the very marked and regular variation of  $n$  from electrolyte to electrolyte. In Table II. below we give the values of  $\Lambda_0$ ,  $B$  and  $n$  at 18° C. for all the electrolytes that we have studied, and Table III. immediately following shows how  $n$  varies with the nature of the electrolyte.

From the data in Table III. it seems quite clear that, so far from being independent of the electrolyte, the exponent  $n$  varies in a perfectly regular manner for electrolytes in a related group. In this table the values of  $B$  and  $n$  are those obtained in the manner just discussed, whilst the columns  $B$  (calc.) and  $n$  (calc.) are obtained by assuming that  $B$  and  $n$  are linear functions of the atomic weights of the cations concerned. Further, the last column of Table II. shows the values of the  $m$  of equation (3) for such substances as we have studied in this connection, and it will be seen that the value of  $m$ , as is indicated in equation (5) is greater than the  $n$  of equation (1) by approximately unity.

It is manifest, then, that the values of  $n$  for the data studied cover a

<sup>9</sup> Ferguson and Vogel, *Phil. Mag.*, 1925, 50, 971. Running, "Empirical Formulæ," 45 (1917).

TABLE II.

Substance.	$\Delta\sigma$	B.	$n$ .	$n$ .
KCl . . . . .	130'04	61'26	0'4520	1'4867
NaCl . . . . .	109'02	54'24	0'4431	1'4763
LiCl . . . . .	99'07	51'74	0'4364	1'4612
KNO <sub>3</sub> . . . . .	126'39	74'67	0'4796	1'4916
NaNO <sub>3</sub> . . . . .	105'48	57'32	0'4458	1'4484
LiNO <sub>3</sub> . . . . .	95'40	47'96	0'4253	1'4465
KIO <sub>3</sub> . . . . .	98'54	61'07	0'4604	1'4566
NaIO <sub>3</sub> . . . . .	77'54	54'66	0'4551	1'4877
LiIO <sub>3</sub> . . . . .	67'53	48'22	0'4422	1'4715
KBr . . . . .	132'30	58'15	0'4324	—
KI . . . . .	130'66	60'86	0'4636	—
KF . . . . .	111'54	56'34	0'4409	—
NaF . . . . .	90'08	62'69	0'4831	—
TiNO <sub>3</sub> . . . . .	127'39	113'10	0'5458	—
TiCl . . . . .	131'04	152'73	0'5763	—
KCNS . . . . .	121'08	74'35	0'4947	—
CsCl . . . . .	133'07	80'97	0'5062	—
AgNO <sub>3</sub> . . . . .	116'19	64'17	0'4404	—
KClO <sub>3</sub> . . . . .	119'57	70'86	0'4747	—
LiClO <sub>4</sub> . . . . .	88'33	103'32	0'6351	—
Ca(NO <sub>3</sub> ) <sub>2</sub> . . . . .	114'02	100'63	0'4196	1'4312
Sr(NO <sub>3</sub> ) <sub>2</sub> . . . . .	113'49	121'72	0'4582	1'4916
Ba(NO <sub>3</sub> ) <sub>2</sub> . . . . .	116'87	175'63	0'5120	1'5436
Pb(NO <sub>3</sub> ) <sub>2</sub> . . . . .	123'44	164'50	0'4520	—
CaCl <sub>2</sub> . . . . .	116'75	115'85	0'4622	—
BaBr <sub>2</sub> . . . . .	126'8	100'9	0'3791	—
MgCl <sub>2</sub> . . . . .	111'63	83'87	0'3991	—
K <sub>2</sub> SO <sub>4</sub> . . . . .	132'85	141'95	0'4582	—
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . . . . .	125'73	324'0	0'6772	—
MgSO <sub>4</sub> . . . . .	113'72	626'2	0'5507	—
CuSO <sub>4</sub> . . . . .	114'16	810'2	0'5711	1'6429
CdSO <sub>4</sub> . . . . .	114'70	771'5	0'5511	1'6487
ZnSO <sub>4</sub> . . . . .	114'26	608'5	0'5271	—

TABLE III.

Substance.	B.	B (calc.).	$n$ .	$n$ (calc.).
LiCl . . . . .	51'74	51'74	0'4364	0'4366
NaCl . . . . .	54'24	55'70	0'4431	0'4452
KCl . . . . .	61'26	59'94	0'4520	0'4539
CsCl . . . . .	80'97	80'97	0'5062	0'5058
LiNO <sub>3</sub> . . . . .	47'96	47'96	0'4253	0'4253
NaNO <sub>3</sub> . . . . .	57'32	62'35	0'4458	0'4522
KNO <sub>3</sub> . . . . .	74'67	74'67	0'4796	0'4596
LiIO <sub>3</sub> . . . . .	48'22	48'22	0'4422	0'4422
NaIO <sub>3</sub> . . . . .	54'66	54'66	0'4551	0'4512
KIO <sub>3</sub> . . . . .	61'07	61'07	0'4604	0'4604
Ca(NO <sub>3</sub> ) <sub>2</sub> . . . . .	100'63	100'63	0'4196	0'4196
Sr(NO <sub>3</sub> ) <sub>2</sub> . . . . .	121'72	137'05	0'4582	0'4643
Ba(NO <sub>3</sub> ) <sub>2</sub> . . . . .	175'63	175'63	0'5120	0'5120

very wide range and, although there is a clustering of the values round about the neighbourhood of 0.5, the differences and the regularities obtaining between these differences are so pronounced that any theory which neglects them must, it seems to us, be regarded as giving at best a

first approximation to the truth. A theory which results in a dilution equation of the form

$$\Lambda = \Lambda_0 - BC^n$$

must take into account regular variations in  $n$  ranging from 0.38 to 0.68 (possibly up to the Ostwald value of approximately unity) and these for what are usually regarded as strong electrolytes.

It follows moreover that a study of the temperature variation of  $B$  and of  $n$  may not be without significance. Most of the data are given for 0°, 18°, and 25° C., and, as far as we can see from the few results which are available the constant  $B$  varies irregularly while  $n$  decreases with rise of temperature save for potassium bromide and sodium acetate. We hope in the future to present the results of some experimental studies in the variation of  $n$  and of  $B$  over a wide range of temperature.

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### GENERAL DISCUSSION.

**Mr. H. Hartley** drew attention to the conclusion of Messrs. MacInnes & Cowperthwaite (p. 404) that the nitrates were not completely dissociated in aqueous solutions; this was in accordance with the results in methyl alcohol solutions for which Dr. Onsager's theory indicated considerable association (p. 348). Similar behaviour was shown by the salts of the alkaline earth metals in methyl alcohol: the perchlorates and chlorides behaved as if they were approximately completely dissociated, while the nitrates behaved like weak electrolytes. With zinc and cadmium on the other hand the perchlorates and nitrates were normal, while the conductivity of the chlorides indicated considerable formation of molecules or complex ions, even in dilute solution. Hence the association was not determined solely by the nitrate ion, but was dependent on the specific relationship between the anion and cation.

**Professor Fajans** said the question had arisen, how far one could look on hydration as being of a chemical or a physical nature. In the interaction between ions one often spoke of a "chemical action" leading to the formation of weak electrolytes, as opposed to the purely electrical action which explained the behaviour of strong electrolytes. Since there was nowadays very little doubt that chemical forces were in the long run to be traced back to physical and especially to electrical forces, it did not seem superfluous to look into the meaning of all this difference. It was certain that the electrostatic interaction of the ions on one another, as well as on the surrounding dipole molecules of water, was accompanied by polarisation phenomena. The cations exerted attractive forces on the electron shells of the anions, or of the water molecules surrounding them, and deformed them to a greater or less extent. He especially wished to point out that the intensity of this action depended not only on the charge and size of the cation, but also on the structure of the electron shell of the cation, as was evident from many properties of the compounds.<sup>1</sup> Thus, the deforming actions of  $Tl^+$  and, particularly, of  $Ag^+$  were incomparably larger than that

<sup>1</sup> Cf. foot-note 1 of page 357.

of  $\text{Na}^+$ . One had then to reckon with the possibility that in those deformations, especially when they were considerable, discontinuities might arise. One could *a priori* distinguish between three cases; the first arose when the strongly deformed electron orbits of the anion or of the water penetrated the electron shell of the cation, the second when the electrons revolved also round the nucleus of the cation. These two cases, however, had a real significance only from the standpoint of the Bohr atomic model, for from the standpoint of the wave mechanics the electron shells, which were distributed throughout space, always penetrated one another and it was only the degree of penetration that could vary continuously with the strength of the deformation. There remained in any case the third possible type of discontinuity, namely that in the union of the ions with one another or with water molecules the quantum numbers of the electrons changed by jumps.

Emphasis of the presence of a "chemical action" of the ions together with the electrical action, could in general mean that one distinguished between cases of strong and of weak deformations, the difference being naturally only a gradual one. A limit could, however, be fixed when one considered on the one hand discontinuous, and on the other continuous, deformation; it was of great interest to seek criteria for the recognition of such discontinuous deformations. Although for that purpose numerous properties of the ions in their compounds had been employed, it seemed to him that, so far, the magnetic properties were the only ones which were not misleading.<sup>2</sup> By union of the strongly paramagnetic  $\text{Fe}^{++}$  with the diamagnetic  $\text{CN}^-$  ion the diamagnetic  $\text{Fe}(\text{CN})_6^{4-}$  was produced. Since paramagnetism was connected with particular quantum states of the ion, there must have taken place in the formation of the complex a far-reaching and discontinuous rearrangement of the electron shells of the components, a "chemical union" of the ions to a new system.

If, however, one considered the many other cases where, by reason of a particular property, a dividing line appeared to exist between electrostatic union of the ions and another kind of union, difficulties were met with. Three only of the most important cases would be mentioned. It was often stated that large changes of light absorption could be regarded as evidence for discontinuous "chemical" action. Since, however, from Hantzsch's<sup>3</sup> investigation the absorption of the iodine ion in solid KI was strongly displaced by the  $\text{K}^+$  towards a shorter wave-length<sup>4</sup> in comparison with that of iodide solutions, such a view could not be held as valid, for in the case of that pronouncedly strong electrolyte one would have to regard the interaction between the ions as a typical non-chemical one. Nor could the hydration of the  $\text{I}^-$  be accompanied by a strong deformation, of which there was as yet no refractometric indication at all.

Recently the lattice type had been proposed as a *criterion* of the kind of union. Grimm and Sommerfeld<sup>5</sup> had shown that in the case of binary compounds the zinc blende and wurtzite lattices, which like the diamond lattice were characterised by a tetrahedral grouping of those lattice points which were closest to one another, only occurred in those cases where

<sup>2</sup> Cf. Fajans and Joos, *Z. Physik*, 1924, 23, 46; Joos, *Ann. Physik*, 1926, 81, 1076; Ladenburg, *Z. physik. Chem.*, 1927, 126, 152. As to another conclusive argument for the changing of the quantum state, in the case, however, of the combination of neutral atoms and not ions, cf. Fajans and Knorr, *Ber.*, 1926, 59, 261.

<sup>3</sup> *Ber.*, 1926, 59, 1096.

<sup>4</sup> Cf. the electrostatic theory of the effect by Herzfeld and Wolf, *Ann. Physik*, 1925, 78, 35, 195.

<sup>5</sup> *Z. Physik*, 1926, 36, 36.

the sum of the valence electrons of the components was 8, *e.g.*, CuCl, AgI, ZnS. It was natural to assume in that case a special kind of union between neutral atoms, similar to that occurring in diamond and different from a union between ions; that appeared also to be indicated by the further necessary condition for the formation of those lattice types, *viz.*, a strong deformability of the anion and a strong deforming action of the cation, the latter being present particularly in the case of ions not of the inert gas type. The deformation of the anion by means of the cation lessened the difference in polarity between the two, and one might suppose that with sufficiently strong deformation the nature of the union changed discontinuously. If, however, one considered the series of substances NaBr, AgBr, AgI, diamond it would appear to be doubtful whether one could take the lattice type as a criterion of the mode of combination. NaBr and AgBr had the NaCl lattice, AgI and diamond the tetrahedral lattice. One would therefore have to fix the limit between the two types of union between AgBr and AgI, whereas from the standpoint of practically all the other physical and chemical properties of those compounds a dividing line must be made between NaBr and AgBr on the one hand, and between AgI and diamond on the other. In AgI the deformation was greater than in AgBr and in the latter much greater than in NaBr. When the deformation was sufficiently strong the lattice type changed, but one could not infer therefrom that the nature of the bond changed discontinuously.

The existence of a more or less sharp limit between weak and strong electrolytes might also be indicated by the fact that, if one neglected acids and bases, the overwhelming majority of soluble salts belonged to the strong electrolyte type and only comparatively few, *e.g.*, some mercury and cadmium salts, formed weak electrolytes. Now undissociability or formation of complexes was only one of the possible manifestations of strong deformation action between the ions. Another possibility was, however, sparing solubility; those salts, which in the solid state manifested considerable deformation actions (*e.g.*, many halides, oxides and sulphides of the heavy metals) could only be obtained in such dilute solutions that so far it had been difficult to say anything about their ability to be dissociated. It could hardly be a coincidence, however, that Dr. Onsager had obtained the largest negative deviations from the theoretical values of the conductivity in the case of  $\text{TlCl}$ . Now the nitrates of the strongly deforming  $\text{Ag}^+$  and  $\text{Tl}^+$  and of several other cations must, as had been pointed out from many sides, for various reasons be looked on as not being completely dissociated. It was, therefore, of interest to mention that in  $\text{NO}_3^-$  one of the O atoms appeared to be relatively easily deformable in comparison with the other two. That was supported by the fact that, although the refraction for one O atom of the nitrate ion was in the average (3.66) equal to that in  $\text{SO}_4^{--}$ , nitric acid, as opposed to sulphuric acid, showed a large decrease of the refraction as the dissociation decreased with increasing concentration. The strong absorption of  $\text{NO}_3^-$  in the near ultraviolet appeared to support that view.

There were wanting therefore, at the present time, sure general criteria for fixing a limit (which could be, even to any extent, sharp) between strong and weak electrolytes, between ionic and atomic combinations, between electrical and "chemical" action of the ions with one another or with water. The conception of deformation, however, made unnecessary that classification into two sharply distinguished groups of compounds and not only explained the actual existence of numerous intermediate states,

but could also in many cases trace back the individual behaviour of the various electrolytes to the particular properties of the constituent ions, *viz.*, charge, size, structure of the electron shell and polarisability.

**Mr. R. H. Fowler** said that according to the newer quantum theory it seemed probable that there would be no sharp distinction between deformation of increasing degrees (as a pair of ions of opposite sign approach) and complete combination to form a neutral molecule. He referred to the recent beautiful considerations advanced by Dr. Hund with special reference to the structure of the ion  $H_2^+$ .<sup>6</sup> It seemed at least in this case that we might expect a continuous gradation of possible forms beginning with free ions at large separation and passing through all degrees of deformation to the most complete union in which the residual external electric field contained a negligible dipole contribution.

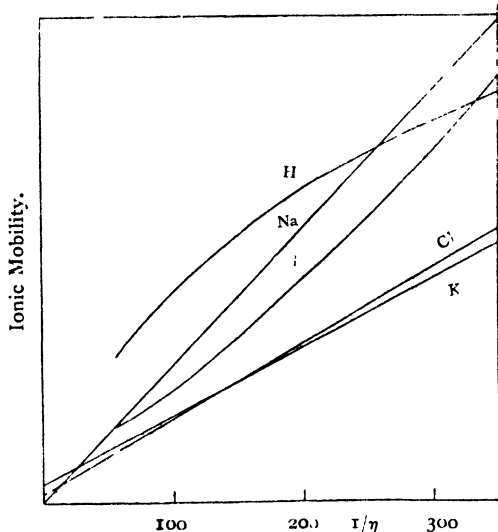


FIG. 1. (See next page.)

There might even be no sharp theoretical dividing line for such systems

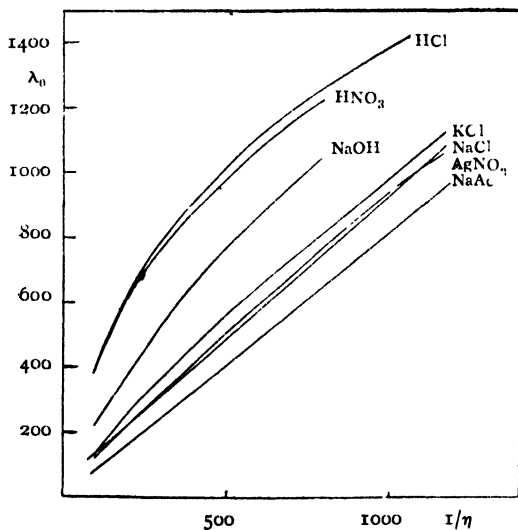


FIG. 2. (See next page.)

into those which would act as conducting systems by separating in an applied field, and those which would not so act. There might merely be a continuous change of the probability of so acting as we pass along the scale of deformation, starting with unity for undeformed ions and ending with zero for the inert molecule. This did not imply that classification into ions which conduct and into neutral molecules which do not was not of great practical importance. Such a classification covered the great majority of examples and

was obviously of fundamental value. The continuous scale of deformations merely implied that we must not be surprised if, on the examination of

<sup>6</sup> *Z. Physik*, 40, 742, 1927; 42, 93, 1927.

exceptional border line examples, we find it impossible to maintain a clear cut classification.

**Mr. R. T. Lattey** said that so much use had been made of Stokes' law in attempting to deduce ionic radii from ionic mobilities that it seemed worth while to examine closely the postulates on which conclusions were often based.

(1) Fig. 1 had been compiled from the best available data in order to test the validity of the statement that  $l/\eta$  in a given solvent is independent of temperature. The solvent chosen was water between  $0^\circ$  and  $100^\circ$ , and it was clear that, with the exception of hydrion, a law of the form  $l = A + B/\eta$  represented the facts.

In Fig. 2 values of  $\lambda_0$  in water had been plotted against fluidity using

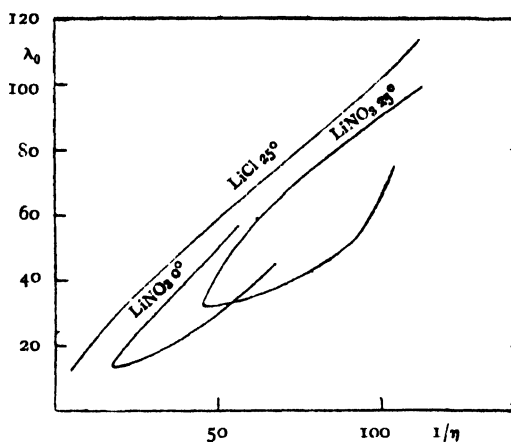


FIG. 3.

Noyes' data (1908) between  $0^\circ$  and  $250^\circ$  C. Except for electrolytes containing  $H^+$  or  $OH^-$  the linear law was obeyed within the limits of experimental uncertainty.

(2) It had been stated that if the solvent were changed then  $\lambda_0\eta$  remained constant. In Fig. 3 Green's values for LiCl in mixtures of sucrose and water and those of Hartley, Applebey, and Garrod Thomas for  $LiNO_3$  in mixtures of pyridine and water had

been plotted. It appeared that the linear law did not apply to the Li ion.

Finally they might take Dutoit and Duperthuis' results for NaI in various organic solvents; the observations did not permit a rigorous test of the linear law but they were not in disagreement with it, *i.e.*,  $\lambda_0\eta = A\eta + B$  where  $A$  is not zero.

#### SODIUM IODIDE IN VARIOUS SOLVENTS.

Solvent.	A.	B.	$\lambda_0\eta$ at $0^\circ$ .	$\lambda_0\eta$ at $40^\circ$ .
Isoamyl alcohol	0.2447	1.76	0.3733	0.2965
Isobutyl "	0.4040	0.49	0.4405	0.4144
Propyl "	0.4459	0.20	0.4532	0.4481
Ethyl "	0.4342	3.90	0.4947	0.4647
Pyridine	0.5540	1.37	0.5725	0.5638
Acetone	0.5522	-12.55	0.5024	0.5169

(3) Stokes' law was derived on the assumption that the fluid in immediate contact with a solid sphere moved with the sphere and that there was a velocity gradient in passing away from the surface of the sphere. The sphere carried a sort of atmosphere of velocity with itself. Now if there were any slipping between the surface of the sphere and the fluid the equation became  $F = 6\pi a\eta v \left\{ \frac{\beta a + 2\eta}{\beta a + 3\eta} \right\}$  whence  $l = \frac{Fe}{6\pi a} \left\{ \frac{1}{\eta} + \frac{1}{\beta a + 2\eta} \right\}$ . If  $\beta a$  were very large this reduced to the simple form  $Fe/6\pi a\eta$ , and it was possibly for this reason that large ions such as anilium and picric acid gave re-

sults consistent with Walden's rule. If on the other hand  $\beta a$  were small then  $l$  approached  $Fe/4\pi\eta a$  and the values of  $a$  calculated in the usual way would approximate to  $3/2$  of the true values, *i.e.* the ion would appear to be larger than it really was and the evidence often adduced for solvation was in reality evidence of slipping which was a form of desolvation.

**Mr. W. F. K. Wynne-Jones** asked Dr. Ulich for the authority for his value of 30.7 for the mobility of the picrate ion in water at 25° C. He stated that the value he himself adopted from the data of Kendall<sup>7</sup> was 34.7. He also quoted some unpublished data for the mobilities of the salicylate, o-nitrobenzoate, cinnamate and hydrocinnamate ions in methyl alcohol, from which it was shown that whereas the viscosity ratio between water and methyl alcohol was 1.64, the inverse mobility ratio was approximately 1.25. He finally asked Dr. Ulich whether in his opinion the accuracy of the data in non-aqueous solutions justified any generalisation such as that of Walden.

(*Added later.*) In conversation with Dr. Ulich, it was found that the value of 30.7 was based upon determinations by Gorke<sup>8</sup> and Busch (unpublished). The discrepancy between the values of such accurate workers as those mentioned above, on the one hand, and of Ostwald and Kendall on the other, suggested the presence of some disturbing influence, possibly adsorption.

In this connection a footnote in a paper by von Halban and Ebert<sup>9</sup> seemed very pertinent.

**Dr. Ulich** replied that in the estimation of the mobility of picrate ions the following measurements were carried out:—

$\Lambda_{\infty}$ of potassium picrate at 18° . . . . .	89.6. <sup>10</sup>
"              "              " . . . . .	89.8. <sup>11</sup>

Therefore it followed that the mobility of the picrate ion at 18° was 25.3 and at 25° (since the validity of Stokes' law between 0 and 100° was established), 29.8. Gorke's measurements in 1908 gave 30.7 at 25°. In their (Dr. Ulich's and those of his co-workers) measurements disturbances due to adsorption had been eliminated since they had worked with both smooth and rough platinum electrodes.

**Professor A. W. Porter** asked, in view of the fact that so many references had been made to viscosity, which viscosity the various speakers had in mind. The conductance of a solution which was nearly rigid owing to the presence of gelatine was very little different from the value when no gelatine was present, although in the former case the viscosity was enormous in comparison.

**Professor Allmand** asked whether it were possible to reconcile the discrepant hydration numbers for certain ions obtained, on the one hand, by considerations of ionic mobility and, on the other hand, from transference data. The  $Li^+$  ion might be taken as an example. The experiments of Dr. Ulich had made it exceedingly likely that this ion, in water, obeyed the Stokes' Law in its ordinary form. From its mobility, and assuming close packing of the water molecules, he had calculated a hydration number of 6. Professor Remy from his transference measurements deduced 12.6. Both pieces of experimental work carried conviction. How could the divergence be explained? Remy's figure held for a  $N$  solution and Ulich's value for infinite dilution, which made the discordance still more striking.

<sup>7</sup> *Proc. Roy. Soc.* (1911), 85A. 200.

<sup>8</sup> *Z. physik. Chem.*, 61, 500 (1908).

<sup>10</sup> *Ibid.*, 106, 49 (1923).

<sup>9</sup> *Ibid.*, 112, 407 (1924).

<sup>11</sup> 1925 unpublished.

**Dr. A. Ferguson and Mr. I. Vogel** (*Communicated*): They had advanced reasons for assuming that the square root concentration law did not adequately represent the facts for strong electrolytes in aqueous solution, but that

$$\Lambda_0 = \Lambda + BC^n$$

represented the facts closely,  $n$  varying in a regular manner among related electrolytes. The extreme range of the values of  $n$  was between (in round numbers) 0.4 and unity, unity being the value demanded for electrolytes conforming to Ostwald's dilution law.

Their own calculations had been confined to aqueous solutions, but it seemed to them advisable to extend them to non-aqueous solution, and one of the writers (I.V.) hoped to publish in the near future the results of such calculations. Meantime they desired to point out that the square root law seemed also to break down under close test for non-aqueous solutions. The Table given below showed the value of  $n$  calculated for two electrolytes in methyl alcohol solution. The data were those of Frazer and Hartley,<sup>12</sup>  $\Lambda$  at round concentrations being interpolated from a large scale conductance-concentration curve. It would be noted that for one of the electrolytes (KI) the value of  $n$  was well away from 0.5, and that the consistency of the values of  $\Lambda_0$  was at least as great, if not greater than the consistency of the values obtained from the square root formula.

KCl in MeOH at 25° C.				KI in MeOH at 25° C.			
Concn. × 10 <sup>-4</sup> .	$\Lambda$ .	$\Lambda_0 = \Lambda$ + 283.9 C <sup>0.8174</sup> .	$\Lambda_0 = \Lambda$ + 261 C <sup>0.8</sup> .	Concn. × 10 <sup>-4</sup> .	$\Lambda$ .	$\Lambda_0 = \Lambda$ + 429.5 C <sup>0.8389</sup> .	$\Lambda_0 = \Lambda$ + 260 C <sup>0.8</sup> .
1	102.37	104.79	104.98	1	112.08	114.06	114.68
2	101.35	104.81	105.04	2	111.11	114.08	114.79
4	99.86	104.81	105.08	4	109.62	114.08	114.82
5	99.25	104.81	105.09	5	108.99	114.07	114.80
8	97.69	104.78	105.07	8	107.44	114.12	114.79
10	96.81	104.77	105.06	10	106.56	114.17	114.78
16	94.63	104.78	105.07				
20	93.43	104.82	105.10				

**Professor Remy** answered that in his opinion ionic mobilities should only be used with great caution in the estimation of the water sheaths of ions. He referred to the extraordinarily large differences between the water sheath calculated by different investigators from ionic mobilities. Riesenfeld<sup>13</sup> for his part had calculated the water sheath of lithium ions to be 158 molecules, Ulich calculated also from mobilities the value 6 molecules. He, Professor Remy,<sup>14</sup> had earlier deduced from mobilities that the water sheath was bound with less than 120 molecules of water. All these very different values applied to infinitely dilute solutions. The value now obtained from water transference numbers, *viz.* 12.6, applied to normal solutions. It was to be expected that the dimension of the water sheath would be larger in infinitely diluted solutions than in normal solutions; how large, however, could not be said with any certainty.

**Dr. Ulich**, in reply, said that the question whether Stokes' law was approximately true for ions did not at present lend itself to theoretical solution; one could only seek to solve it experimentally. For this purpose measurements, such as Mr. Lattey had cited, in mixed solvents were hardly suitable, since these solvents were not homogeneous in their viscosity; the measured macroscopic viscosity was only decisive in the case of very large ions (*cf.* the remarks of Professor Porter). Green's measurements proved this most clearly.

<sup>12</sup> *Proc. Roy. Soc.*, 1925, 109, A., 351.

<sup>13</sup> *Z. physikal. Chem.*, 1909, 66, 672.

<sup>14</sup> *Ibid.*, 1915, 89, 467.

On the other hand one could draw conclusions as to the validity of Stokes' law from the temperature relations of ionic mobilities, provided of course that use were made or by the mobilities or conductivities extrapolated to infinite dilution, so that no disturbances due to other temperature effects (such as alteration of the specific conductivity with temperature and dielectric constant) were introduced. Dutoit and Duperthuis, from whose tables Mr. Lattey had given an extract, had sought to obtain experimentally the limiting values of molecular conductivity at dilutions of 1000 to 20,000 litres, a proposal which had since been proved untenable. Nevertheless the limiting values of  $\lambda_0\eta$  so obtained had been cited by Mr. Lattey. Walden had shown on the other hand about 1911<sup>15</sup> that one obtained a better temperature constant of  $\Lambda_\infty\eta$  from the limiting values of conductivities extrapolated from the measurements of Dutoit and Duperthuis in the usual way. He (Dr. Ulich) had recently collated a large amount of material from the literature.<sup>16</sup> It appeared that in alcohol, nitromethane, acetone, pyridine,  $\text{SO}_2$  and other solvents the product  $\Lambda_\infty\eta$  was in every known case constant with temperature, within the limits of error; in water also there were a number of cases (including  $\text{Li}^+$ ) in which the same condition applied.

Now the constancy to temperature of  $\Lambda_\infty\eta$  was naturally only one result of Stokes' law, but one might seek by reason of this confirmation to show the approximate validity of the law for ions if they exhibited this temperature constancy. (He, Dr. Ulich, had shown that the point was no better demonstrated in the case of generalisations from the friction laws, as derived by Cunningham and others.) Ionic radii calculated with the help of Stokes' law in this way and in such cases had a definite physical meaning.

The ionic mobilities which he had tabulated were by no means adduced from such theoretical considerations, they were founded entirely on experimental data, namely, on the proved strict validity of the Walden rule ( $\Lambda_\infty\eta$  independent of the solvent) for salts consisting of large ions. All organic ions were not, however, necessarily large in this sense and especially not so in the case of the anions of carboxylic acids such as those mentioned by Mr. Wynne-Jones; the size of the whole ion was obviously less important than the size and arrangement of the substituting groups ( $\text{COO}^-$  in this case). The size of carboxylic ions was, from the point of view of solvation, not independent of the nature of the solvent.

As to the reason for the discrepancy between his own figures and those of Professor Remy for the hydration numbers of  $\text{Na}^+$  and  $\text{Li}^+$  he thought that a very trustworthy calculation was not possible by his method, especially since the nature of the packing within the sheath and the true volume of the solvent molecule were unknown. They might well expect errors of  $\pm 50$  per cent. On the other hand it was quite conceivable that from the nature of the experimental methods Professor Remy's figures for water sheaths not only took into account the true closely bound hydrate water, but also included to some extent the hydrodynamic and circulating water. Professor Remy's higher figures would be explained thus. This seemed probable also by reason of Professor Remy's very unexpected results, that the values rose to nearly double when passing from  $\text{H}_3\text{N}(\text{CH}_3)^+$  (2.4) to  $\text{N}(\text{CH}_3)_4^+$  (4.6) or  $\text{H}_3\text{N}(\text{C}_3\text{H}_7)^+$  (5.5). On the whole he (Dr. Ulich) thought that the differences between his own and Professor Remy's hydration numbers did not exceed the experimental errors associated with their measurements and calculations.

<sup>15</sup> *Z. physik. Chem.*, 78, 271.

<sup>16</sup> *Beweglichkeit der elektrolytischen Ionen, Fortschritte der Chemie, Physik u physikal. Chemie.*

INTRODUCTORY PAPER.—PART II : ACTIVITY.  
ON THE ACTIVITY OF ELECTROLYTES.

By J. N. BRÖNSTED.

*Received March 26th, 1927.*

1. Introduction.

The modern form of the Arrhenius theory of electrolytic dissociation originates in the fact that the apparently anomalous behaviour of strong electrolytes cannot be explained satisfactorily on the basis of the van't Hoff law of dilute solutions and the classical mass action law. The realisation of this impossibility dates back to the beginning of this century<sup>1</sup> and at about the same time the first attempts were made to explain the behaviour of strong electrolytes by considering them as practically completely ionised and assuming that the electric forces between the ions are responsible for the anomalies observed.

Thus van Laar,<sup>2</sup> Sutherland<sup>3</sup> and Bjerrum<sup>4</sup> from different points of view suggested the dissociation of strong electrolytes to be much larger than appears from the usual calculations on the basis of conductivity data. Milner<sup>5</sup> in 1913 made an attempt to calculate quantitatively the effect of the ionic forces on the thermodynamic functions of a salt solution. Mathematical difficulties impeded a strict solution of the problem, but the approximate results showed a surprisingly good agreement with the experimental data and strongly favoured the theory of complete dissociation.

In 1916 Bjerrum<sup>6</sup> developed further his earlier deductions and presented several aspects for the theoretical and experimental treatment of the problem. His adoption of the osmotic and activity coefficients as functions fitted for describing the behaviour of salt solutions has proved very serviceable. From this time begins a more intensified study of salt solutions from the point of view of the interionic attraction and complete dissociation theory.

2. The Thermodynamic Laws of Salt Solutions.

An ideal or perfect solution may be defined as a solution for which an expression such as

$$\bar{F}_1 = RT \ln x_1 + I_1 \quad . \quad . \quad . \quad . \quad (1)$$

holds for each of its components at constant temperature and pressure.  $\bar{F}_1$  is the differential or partial molal free energy,<sup>7</sup>  $x_1$  the mol fraction, and  $I_1$

<sup>1</sup> See the discussion of the problem of the strong electrolytes by Jahn, Nernst and Arrhenius, *Z. physik. Chem.*, **33** (1900)—**38** (1901).

<sup>2</sup> Van Laar, *Arch. Teylor* (2) **7**, 1, 1 (1900).

<sup>3</sup> Sutherland, *Phil. Mag.*, **14**, 1 (1907).

<sup>4</sup> Bjerrum, *Proc. 7th Intern. Congr. Pure and Applied Chem.*, X. (1909).

<sup>5</sup> Milner, *Phil. Mag.*, **23**, 551 (1912); **25**, 743 (1913).

<sup>6</sup> Bjerrum, *Fysisk Tidsskrift*, **15**, 59 (1916); *Z. Elektrochemie*, **24**, 231 (1918).

<sup>7</sup> Lewis and Randall, "Thermodynamics," p. 203 (1923).

an arbitrary constant. This equation holds for a dilute non-electrolytic solution.

For an electrolytic solution the equation does not hold at ordinary concentrations. By writing instead of (1):

$$\bar{F}_1 = RT \ln a_1 + I_1 \quad . \quad . \quad . \quad . \quad (2)$$

G. N. Lewis defines an important new function  $a$  called the activity<sup>8</sup> which, also in the case of ions, is proportional to concentration in sufficiently dilute solution.

Since  $x$ , the mol fraction, and  $m$ , the molality, are proportional in dilute solution, either  $a = x$  or  $a = m$  may be taken as limiting relations to standardise the numerical value of the activity.

$F$  and  $a$  are in principle identical in describing the deviations of salt solutions from the ideal conditions. The practical superiority of the activity function in most cases depends upon its simpler relationship to the concept of concentration.

The ratio of activity to concentration,

$$f = \frac{a}{x} \quad \text{or} \quad f = \frac{a}{m}$$

is called the *activity coefficient* or activation<sup>9</sup> and is the most direct measure of the ionic abnormalities. The utility of this conception has been particularly demonstrated by Lewis in his fundamental studies on salt solutions. The activity coefficients are correlated thermodynamically by the equation,

$$\sum x_1 d \ln f_1 = 0 \quad . \quad . \quad . \quad . \quad (3)$$

This equation applies directly to ions as constituents of the solution. In case salts are taken as constituents we have to introduce  $\nu \ln f = \sum \nu_1 \ln f_1$ ,  $f$  being the activity coefficient of the salt,  $f_1, f_2 \dots$  of the ions and  $\nu = \nu_1 + \nu_2 \dots$  the number of ions formed by dissociation of one molecule of salt.

An ideal dilute solution can also be defined as a solution for which the van't Hoff factor  $i$ , derived for instance by freezing-point measurements, equals the number of ions  $\nu$  formed by complete dissociation of a salt molecule. The deviations from ideal conditions can be measured by the ratio:

$$\phi = \frac{i}{\nu}$$

called the *osmotic coefficient*. If the solvent is characterised by the subscript 0 we have:

$$\bar{F}_0 = - RT x \phi = RT \ln(1 - x) f_0$$

where  $x = \sum x_1$ , or

$$\ln f_0 = x(1 - \phi) \quad . \quad . \quad . \quad . \quad (4)$$

This equation introduced into (3) gives us a generalisation of the relation between osmotic and activity coefficients first given by Bjerrum.<sup>10</sup>

$$x \frac{d\phi}{dx} + \phi = \sum x_1 \frac{d \ln f_1}{dx} + 1 \quad . \quad . \quad . \quad . \quad (5)$$

<sup>8</sup> Lewis, *Proc. Am. Acad. Sc.*, **43**, 259 (1907); *Z. physik. Chem.*, **61**, 129 (1910).

<sup>9</sup> Noyes, A. A., *J. Am. Chem. Soc.*, **46**, 1080 (1924).

<sup>10</sup> For a more detailed treatment of the thermodynamic relationships for these functions, see Bjerrum, *Z. physik. Chem.*, **104**, 406 (1923).

<sup>19</sup> Brönsted and LaMer, *J. Am. Chem. Soc.*, **44**,

Salt.	$-\log f.$
HCl . . .	$0.5\sqrt{m} - 0.60 m$
LiCl . . .	$0.5\sqrt{m} - 0.50 m$
NaCl . . .	$0.5\sqrt{m} - 0.49 m$
KCl . . .	$0.5\sqrt{m} - 0.40 m$
KOH . . .	$0.5\sqrt{m} - 0.46 m$

Except in the case of hydrochloric acid the expressions agree excellently up to 0.1 M. solution, with the experimental data as recalculated by Scatchard. For HCl the agreement is somewhat less satisfactory, the data being better fitted by a somewhat smaller  $\alpha$ -value ( $-\log f = 0.45\sqrt{m} - 0.5m$ ).<sup>21</sup> The  $\beta$ -coefficient 0.50 for LiCl may also be to some extent inaccurate in view of the fact that it does not correspond well with the interaction data of Güntelberg.<sup>18</sup> It should be noted that this individual member in 0.1 M. solution accounts for about  $\frac{1}{3}$  of the total deviation of  $f$  from unity.

For the general case of an arbitrary ion present in an arbitrary dilute salt solution, the theory of Lewis and Randall<sup>22</sup> concerning the conception of *ionic strength* is applicable. The ionic strength is defined as  $\frac{1}{2}\sum m_i z_i^2 = \frac{1}{2}\sum c_i z_i^2$ , where  $m$  is molality,  $c$  equivalent concentration, and  $z$  valence of any ion present in the solution, and the generalisation offered by Lewis and Randall is that in dilute solution the activity of a given ion is the same in all solutions of the same ionic strength. This generalisation is not true in regions of concentration where the individual differences become evident, but has to be looked upon as a limiting law for great dilution. This principle in connection with the limiting equation for uni-univalent salts and the influence of the valence of the ion considered gives

$$-\ln f = Az^2\sqrt{\mu} \quad . \quad . \quad . \quad (10)$$

as the general limiting expression for the activity coefficient of any ion in a salt solution of any type.

At somewhat higher concentration and constant type of the solvent solution the expression should be:

$$-\ln f = Az^2\sqrt{\mu} + B\mu \quad . \quad . \quad . \quad (11)$$

B accounting for the individuality of the system considered.

Equation (10) was recently verified by Brönsted and Brumbaugh<sup>23</sup> by solubility measurements using a tri-tri-valent salt of molal solubility about  $10^{-5}$  in NaCl as solvent. Up to about 0.01 M. solution the data are represented by

$$-\log f = 0.45z^2\sqrt{\mu}$$

i.e.,  $A = 0.45$ .

Similar results were obtained for NaCl by LaMer, King and Mason<sup>24</sup> while with  $\text{KNO}_3$  as a solvent these authors found the somewhat higher  $A$ -value 0.52. Their data at higher concentration of the solvent salt are expressible by equation (11), the validity of which is corroborated also by using other experimental methods.

<sup>21</sup> See also, Nonhebel, *Phil. Mag.* 7, 2, 1085 (1926).

<sup>22</sup> Lewis and Randall, *J. Am. Chem. Soc.*, 43, 1140 (1921).

<sup>23</sup> Brönsted and Brumbaugh, *J. Am. Chem. Soc.*, 48, 2015 (1926).

<sup>24</sup> LaMer, King and Mason, *J. Am. Chem. Soc.*, 49, 363 (1927).

On the whole, equation (10) with the value of  $A$  not far from 0.5 seems to express a limiting law for the activity coefficient in any dilute mixture of salts, while the deviation from this limiting law depends upon the nature of the ions present and varies linearly with their concentration.

Apparent anomalies, referred to as the electric type effect, in mixtures of ions of high and opposite valence noted by Brönsted and Petersen<sup>25</sup> and Brönsted and LaMer,<sup>26</sup> and quite recently the subject of a more detailed study from the standpoint of the Debye Theory (Section 4) by LaMer and Mason<sup>27</sup> deserve special consideration.

### 3. The Principle of Specific Interaction.

The individualities of salt solutions, as represented by the coefficient  $\beta$  in equation (8), are apparently of a complex nature. From the freezing-point difference of 0.1 M. NaCl and KCl solutions, for instance, we cannot determine the corresponding difference for the nitrates. In each particular case the properties exhibited seem to depend on the special combination of ions considered.

In so far as an electric interaction is the source of these individualities there are good reasons to refer them to an interaction between ions of opposite sign, since these may approach to small distances, while owing to the repelling forces the effect of ions of the same sign upon each other can be taken as uniform, depending only on their charges. In addition to this electric interaction, however, we must expect the ions also to be exposed to a general salting out effect, which may be considered in a first approximation as depending only on the nature and concentration of the solvent ions. These ideas are the basis of the *principle of the specific interaction of ions*.<sup>28</sup>

For instance, in the case of a hydrogen ion, present in slight concentration in a potassium nitrate solution, say 0.1 M., from this point of view we can write for the activity coefficient,

$$f_{H(KNO_3)} = f_{H(K)} f_{H(NO_3)} f_{(K)} f_{(NO_3)},$$

where  $f_{H(K)}$  and  $f_{H(NO_3)}$  represents the interaction coefficients and  $f_{(K)}$  and  $f_{(NO_3)}$  the salting out coefficients of the solvent ions. If the solvent is a sodium nitrate solution of the same concentration, the activity coefficient of the hydrogen ion is similarly :

$$f_{H(NaNO_3)} = f_{H(Na)} f_{H(NO_3)} f_{(Na)} f_{(NO_3)}.$$

Hence, since according to our principle  $f_{H(K)} = f_{H(Na)}$  :

$$\frac{f_{H(NaNO_3)}}{f_{H(KNO_3)}} = \frac{f_{(Na)}}{f_{(K)}} \quad . \quad . \quad . \quad . \quad (12)$$

*i.e.*, the activity coefficient ratio of a positive ion in two solutions with a common anion is independent of the nature of the positive ion considered and also independent of the nature of the common anion of the solvent salt.

For a chloride ion in the same solutions the corresponding expression is

$$\frac{f_{Cl(NaNO_3)}}{f_{Cl(KNO_3)}} = \frac{f_{Cl(Na)}}{f_{Cl(K)}} \frac{f_{(Na)}}{f_{(K)}} \quad . \quad . \quad . \quad . \quad (13)$$

<sup>25</sup> Brönsted and Petersen, *J. Am. Chem. Soc.*, **43**, 2265 (1921).

<sup>26</sup> Brönsted and LaMer, *ibid.*, **46**, 555 (1924).

<sup>27</sup> La Mer and Mason, *J. Am. Chem. Soc.*, **49**, 410 (1927).

<sup>28</sup> Brönsted, *J. Am. Chem. Soc.*, **44**, 877 (1922); **45**, 2898 (1923).

and for HCl, defining  $f_{\text{HCl}}$  by the equation  $f_{\text{HCl}}^2 = f_{\text{H}} f_{\text{Cl}}$ :

$$\frac{f_{\text{HCl}(\text{NaNO}_3)}}{f_{\text{HCl}(\text{KNO}_3)}} = \left( \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} \right)^{\frac{1}{2}} \frac{f_{\text{(Na)}}}{f_{\text{(K)}}} \quad (14)$$

The coefficients  $f_{\text{H}}$  and  $f_{\text{NO}_3}$  do not enter into this ratio and consequently the activity coefficient ratio for a dissolved salt in two solvents having an anion in common, is independent of the cation of the solute and the anion of the solvent. A corresponding rule of course holds if the two solvents have a common cation.

These relationships have been derived here particularly for solvent salts of the same type. They are easily generalised when it is realised on the basis of our principles that such a ratio as

$$\frac{f_{\text{K}(\text{Na})}}{f_{\text{K}(\text{Ba})}},$$

for the same equivalent concentration is a function determined merely by the type of the solute and solvent salt.

The relations thus obtained have been amply verified by means of solubility measurements, and lately by Guntelberg<sup>18</sup> by very accurate solubility and electrometric measurements. The following figures give his

values for  $\log \frac{f_{\text{HCl}(\text{HCl})}}{f_{\text{HCl}(\text{XCl})}} = \log (\text{I.})$  (second column) electrometrically deter-

mined and  $\log \frac{f_{\text{OCl}(\text{HCl})}}{f_{\text{OCl}(\text{XCl})}} = \log (\text{II.})$  (third column) determined by solubility

measurements. X represents the series of alkali metals and O is a complex univalent cobaltammine cation. The concentration of XCl is 0.1 mol.

Solvent Salt.	Log (I.).	Log (II.).
HCl . . .	0.0000	0.0000
LiCl . . .	0.0007	0.0006
NaCl . . .	42	39
KCl . . .	84	84
CsCl . . .	146	147

showing the strict validity of the principle.

By means of the principle of specific interaction, it is also possible to correlate activity coefficients of dissolved salts with the osmotic coefficients of the salt solution serving as solvent. Applying equations (3) and (4) in the form,

$$\sum m_i d \ln f_i = m d \phi \quad (15)$$

to a mixture of say NaCl and KCl of total concentration  $m$ , putting  $m_{\text{NaCl}} = mx$ , and  $m_{\text{KCl}} = m(1-x)$  we obtain:

$$x d \ln f_{\text{Na}} + (1-x) d \ln f_{\text{K}} + d \ln f_{\text{Cl}} = 2 d \phi.$$

Introducing, by the principle,  $d \ln f_{\text{Na}} = d \ln f_{\text{K}} = d \ln f_{\text{X}}$ , X being an arbitrary univalent cation, (15) becomes:

$$d \ln f_{\text{X}} + d \ln f_{\text{Cl}} = 2 d \phi$$

or

$$\ln \frac{f_{\text{XCl}(\text{NaCl})}}{f_{\text{XCl}(\text{KCl})}} = \phi_{\text{NaCl}} - \phi_{\text{KCl}} \quad (16)$$

Thus, determinations of  $f_{\text{HCl}}$  in NaCl and KCl solutions by E.M.F. measurements enables us to calculate the difference in freezing-points of the two solutions and *vice versa*.

Several of these results are obtainable on the simple assumption of a linear change in  $\ln f$  with the ratio NaCl/KCl at constant total concentration.<sup>28</sup> Such a linear change has been found at 0.1 mol. solution by Güntelberg<sup>18</sup> and in more concentrated solutions by Harned.<sup>29</sup>

Still a further step can be taken. From equations (8) and (9),

$$\begin{aligned} 1 - \phi &= a\sqrt{m} + \beta m \\ - \ln f &= 3a\sqrt{m} + 2\beta m \end{aligned}$$

we see that

$$\phi_1 - \phi_2 = \frac{1}{2} \ln \frac{f_1}{f_2} \quad . \quad . \quad . \quad (17)$$

and therefrom by means of (16)

$$\ln \frac{f_{\text{HCl(NaCl)}}}{f_{\text{HCl(KCl)}}} = \frac{1}{2} \ln \frac{f_{\text{NaCl}}}{f_{\text{KCl}}} \quad . \quad . \quad . \quad (18)$$

Scatchard<sup>20</sup> in his critical study of the activity coefficients mentioned above gives for 0.1 molal solution  $f_{\text{NaCl}} = 0.778$ ,  $f_{\text{KCl}} = 0.762$ , hence:

$$\frac{1}{2} \log \frac{f_{\text{NaCl}}}{f_{\text{KCl}}} = 0.0045$$

while from Güntelberg's electrometric data,<sup>18</sup>

$$\log \frac{f_{\text{HCl(NaCl)}}}{f_{\text{HCl(KCl)}}} = 0.0042.$$

Equation (18) is thus strictly verified. For HCl and particularly LiCl in conjunction with NaCl or KCl the agreement is not so satisfactory, and the corresponding data are therefore to be looked upon as yet to some extent open to doubt.

It should be noted that the principle of specific interaction emphatically contradicts the classical explanation of individual behaviour of salts as due to difference in degree of dissociation.

#### 4. Theoretical Calculation of Activity Coefficients.

The attempt by Milner<sup>5</sup> to calculate theoretically the osmotic pressure of a salt solution was, as mentioned above, impaired by mathematical difficulties. The theory of Ghosh<sup>30</sup> based upon a very simplified conception of the constitution of a salt solution has proved to be unsatisfactory. Bjerrum<sup>31</sup> on the basis of the idea that the approach of ions to each other is controlled by their size estimated the osmotic pressure in solutions of moderate concentration. Finally, Debye and Hückel,<sup>32</sup> worked out an apparently very successful theory for dilute salt solutions which has been the centre of interest in the more recent study of electrolytes.

The fundamental reasoning underlying the Debye-Hückel theory is as follows. Due to the Coulomb forces the "ionic atmosphere" surrounding any selected positive ion will contain an excess of negative electricity. This will cause an average electric potential  $\psi$  and an average electric

<sup>28</sup> Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

<sup>29</sup> Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707, 790 (1918); *Z. Physik. Chem.*, **98**, 211 (1921).

<sup>31</sup> Bjerrum, *Z. anorg. Chem.*, **120**, 323, (1923).

<sup>32</sup> Debye and Hückel, *Physik. Z.*, **21**, 185 (1923).

density  $\rho$ , different from zero, to exist in any distance from the selected ion, the total potential and density being interrelated by the Boltzmann distribution principle and the Poisson equation. Hence for a solution of the KCl type

$$\rho = n\epsilon \left( e^{-\frac{e\psi}{kT}} - e^{\frac{e\psi}{kT}} \right) \quad . \quad . \quad . \quad (19)$$

$$\nabla^2 \psi = - \frac{4\pi\rho}{D} \quad . \quad . \quad . \quad (20)$$

where  $\epsilon$  is the charge of a positive univalent ion,  $k$  the Boltzmann constant,  $T$  the temperature,  $D$  the dielectric constant, and  $n$  the number of positive ions in 1 c.c. Eliminating  $\rho$  we obtain

$$\nabla^2 \psi = - \frac{4\pi n\epsilon}{D} \left( e^{-\frac{e\psi}{kT}} - e^{\frac{e\psi}{kT}} \right) \quad . \quad . \quad . \quad (21)$$

or

$$\nabla^2 \psi = \frac{8\pi n\epsilon}{D} \sinh \frac{\psi\epsilon}{kT} \quad . \quad . \quad . \quad (22)$$

from which  $\psi$  is determined.

Since the average potential in the space around the selected ion depends only upon the distance  $r$  from it, equation (22) for small potentials for which  $\frac{\psi\epsilon}{kT}$  can be substituted for  $\sinh \frac{\psi\epsilon}{kT}$ , becomes

$$\frac{d^2\psi}{dr^2} + \frac{2}{r} \cdot \frac{d\psi}{dr} = \kappa^2 \psi \quad . \quad . \quad . \quad (23)$$

where

$$\kappa^2 = \frac{8\pi\epsilon^2 n}{kDT} \quad . \quad . \quad . \quad (24)$$

$\frac{1}{\kappa}$ , which has the dimension of a length, is called the thickness of the ionic atmosphere and is a characteristic quantity in the theory.

On integration :

$$\psi = A \cdot \frac{e^{-\kappa r}}{r} \quad . \quad . \quad . \quad (25)$$

where  $A$  is a constant. From this equation we are able to find the potential at a very small distance from the selected ion :

$$\psi = \frac{A}{r} - A\kappa \quad . \quad . \quad . \quad (26)$$

or since this equation represents the total potential due to both the ion itself and the ionic atmosphere, the first of which being  $\frac{\epsilon}{Dr}$ , where  $D$  is the dielectric constant, for the potential due to the ionic atmosphere on the place of the selected ion we can write :

$$\psi = - \frac{\epsilon\kappa}{D} \quad . \quad . \quad . \quad (27)$$

This equation satisfies evidently the obligatory condition that for infinitely high temperatures or infinitely small concentrations the potential should vanish.

If the solution is not of the simple KCl type but any mixture of ions of different concentration and valence, the expression for  $\kappa$  becomes

$$\kappa^2 = \frac{4\pi\epsilon^2}{kDT} \sum n_j z_j^2 \quad . \quad . \quad . \quad (28)$$

$n_j$  being the number and  $z_j$  the valence of the ions of the  $j^{\text{th}}$  sort, and the expression for the potential of an ion of the  $i^{\text{th}}$  sort:

$$\psi_i = - \frac{\epsilon z_i \kappa}{D} \quad . \quad . \quad . \quad (29)$$

This is the fundamental equation in the theory. In the derivation we have only made use of the average potential  $\psi$  and average density of electricity  $\rho$ , instead of considering the individual configurations of electric distribution. This is permissible so long as  $\sinh \frac{\psi\epsilon}{kT}$  can legitimately be

replaced by  $\frac{\psi\epsilon}{kT}$ . If this is no longer the case, for instance when the ions are too small or concentration too high, the theory loses its strict character and is only applicable as an approximation.<sup>33</sup> The influence of changes in the dielectric properties in the neighbourhood of the ions have been shown by Debye and Pauling<sup>34</sup> to be insignificant for the ideal value of  $\psi$ .

From the potential  $\psi$  it is possible to determine the thermodynamic functions of the solution by a number of methods. We shall confine ourselves to the study of solutions of uni-univalent salts since all the characteristics of the methods appear just as well in this simple case. The most easy method is possibly to calculate first the differential electric free energy  $\bar{F}_1$  of one ion by the method of Guntelberg.<sup>18</sup>  $\bar{F}_1$  equals the electric work done by the system when the charge of a positive ion is brought to infinite dilution where the  $\psi$ -potential by definition is zero. When the discharging process is carried out gradually  $\kappa$  will not change, and therefore since the potential is proportional to the charge:

$$\bar{F}_1 = \frac{\psi\epsilon}{2} = - \frac{\epsilon^2 \kappa}{2D} \quad . \quad . \quad . \quad (30)$$

From the definition  $\bar{F}_1 = kT \ln f$  we obtain then for the activity coefficient:

$$\ln f_1 = \frac{\psi\epsilon}{2kT} = - \frac{\epsilon^2 \kappa}{2DkT} \quad . \quad . \quad . \quad (31)$$

and for the osmotic coefficient since equation (31) is in conformity with equation (9):

$$\phi - 1 = \frac{\psi\epsilon}{6kT} = - \frac{\epsilon^2 \kappa}{6DkT} \quad . \quad . \quad . \quad (32)$$

From equation (30) combined with the Gibbs-Duhem equation or directly from equation (32) and:  $\bar{F}_0 = - \frac{kT 2 n_1}{n_0} (\phi - 1)$  (in which  $F_0$  is the differential electric free energy of the solvent,  $n_0$  the number of solvent molecules, and  $n_1$  the number of positive ions in one c.c.), we obtain for the electric differential free energy of one molecule of the solvent:

$$\bar{F}_0 = \frac{n_1}{n_0} \frac{\epsilon^2 \kappa}{3D} = - \frac{n_1}{n_0} \frac{\psi\epsilon}{3} \quad . \quad . \quad . \quad (33)$$

<sup>33</sup> See Fowler, *Trans. Cambr. Phil. Soc.*, **22**, 861 (1925).

<sup>34</sup> Debye and Pauling, *J. Am. Chem. Soc.*, **47**, 2129 (1925).

and for the total electric free energy of one c.c. of solution :

$$F = 2n_1\bar{F}_1 + n_0\bar{F}_0$$

$$F = -\frac{2n_1\epsilon^2\kappa}{3D} = \frac{2n_1\psi\epsilon}{3} \quad . \quad . \quad . \quad (34)$$

Expression (34) for the total electric free energy of the salt solution can also be obtained directly from equation (30) on integration and, furthermore, as shown by Debye,<sup>35</sup> by considering the process of discharging all the ions simultaneously. Since in this process the potential  $\psi$  changes proportionally to the square of the charge, integration gives for one ion  $\frac{\psi\epsilon}{3}$  in conformity with (34).

In the original paper of Debye and Hückel,  $F$  was calculated from  $\psi$  by first determining the "electric energy," defined in the following way.

Presume the thermal movement of the ions in a solution be stopped simultaneously for all of the ions. The solution will be what we shall call a "constrained solution" which is of course entirely different from a "natural solution." In calculating the work of continuously discharging such a solution in conformity with the Debye consideration above, the  $\kappa$ -function is not applicable. Since, however, when all ions are discharged simultaneously the potential  $\psi$  is proportional to the charge, the work for one ion is

$$A = \frac{\psi\epsilon}{2} = -\frac{\epsilon^2\kappa}{2D} \quad . \quad . \quad . \quad (35)$$

i.e.,  $3/2$  the work for discharging the natural solution.  $A$  is the "electric energy." This result is also obtained by discharging the ions one after another in a surface layer. The potential in the surface must be only half of the potential in the interior of the solution and does not vary during the discharging process.  $A$ , therefore, also according to this consideration is given by (35).

Free and total energy are correlated thermodynamically by the equation :

$$F = -T \int_U \frac{dT}{T^2} \quad . \quad . \quad . \quad (36)$$

Introducing for  $U$  the electric energy  $A$ , on integration from  $T$  to  $\infty$  the dielectric constant should be kept constant<sup>36</sup> in which case expression (34) follows. This is the original Debye-Hückel method.

In a direct thermodynamic calculation, however, for  $U$  in equation (36) should be introduced the total energy which is computable from the thermodynamic equation,

$$A - U = T \frac{dA}{dT} \quad . \quad . \quad . \quad (37)$$

$A$  is certainly different from what usually is called a free energy, in fact the idea of a constrained system is contradictory to the second law of thermodynamics. From the convention, however, that the constrained system shall be left in unchanging constrained condition during the whole discharging operation and temperature changes,  $A$  can be taken as a free energy and equation (37) becomes applicable.

<sup>35</sup> Debye, *Physik. Z.*, **25**, 97 (1924).

<sup>36</sup> Gross and Halpern, *Physik. Z.*, **26**, 403 (1925).

Adams, *J. Am. Chem. Soc.*, **48**, 621 (1926).

From this, since for any constrained system AD is a constant independent of temperature :

$$U = \frac{A}{D} \frac{d(DT)}{dT} = A \left( 1 + \frac{d \ln D}{d \ln T} \right) \quad . \quad . \quad . \quad (38)$$

Introducing this expression for U and expression (35) for A in equation (36)\* the free energy is calculated in concordance with (34). This is in substance the method of Bjerrum.<sup>37</sup>

According to E. Q. Adams<sup>36</sup> for H<sub>2</sub>O from 10° to 100°  $\frac{d \ln D}{d \ln T} = -1.5$  and so for the total energy (heat of dilution) for one ion we can write :

$$U = \frac{\epsilon^2 \kappa}{4D},$$

having half the value and opposite sign of the electric energy.

It should be mentioned that the equation for the osmotic pressure and free energy on the basis of the Debye-Hückel theory is obtained by A. A. Noyes<sup>9</sup> by using the Clausius virial equation.

In order to test the theory experimentally we introduce numerical values in the equations. We obtain then from equation (24), (31), and (32) :

$$\kappa = 5.03 \cdot 10^9 \sqrt{\frac{m}{DT}} \quad . \quad . \quad . \quad (39)$$

$$- \log f_1 = 1.815 \cdot 10^6 \frac{\sqrt{m}}{(DT)^{\frac{3}{2}}} \quad . \quad . \quad . \quad (40)$$

$$1 - \phi = 1.393 \cdot 10^6 \frac{\sqrt{m}}{(DT)^{\frac{3}{2}}} \quad . \quad . \quad . \quad (41)$$

For water as solvent and the general case of an ion of valence  $z$  in an arbitrary solution :

$$- \log f_{(10^\circ)} = 0.486 z^2 \sqrt{\mu} \quad . \quad . \quad . \quad (42)$$

$$- \log f_{(20^\circ)} = 0.505 z^2 \sqrt{\mu} \quad . \quad . \quad . \quad (43)$$

where  $\mu$  is the ionic strength as defined above. Comparison of these equations with the empirical equations for  $f$  presented in Section 2 furnishes a striking verification of the Debye-Hückel theory in the range of great dilution. Also at higher temperatures the theory seems to hold as shown by Baxter<sup>38</sup> on the basis of solubility measurements at 75°. Other evidence in favour of it is obtained in the field of weak electrolytes.

Equation (29) for the atmospheric potential and the equations based thereupon are limiting laws for great dilution. For higher concentrations, when the effect of closely approaching ions is no longer negligible, the distance to which these may approach would obviously come into play. This involves consideration of ionic "sizes." Taking the ions as spheres of diameter  $a$  with the charge in the centre and possessing the same dielectric constant  $D$  as the solvent the theory leads to the following expression for the potential :

$$\psi = - \frac{\epsilon \kappa z}{D} \cdot \frac{1}{1 + \kappa a} \quad . \quad . \quad . \quad (44)$$

\* This equation gives for  $U = BT^n$  the general solution  $F = - \frac{B}{1-n} T^n + iT$ ,

$i$  in the present case being zero.

<sup>37</sup> Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926).

<sup>38</sup> Baxter, *J. Am. Chem. Soc.*, **48**, 615 (1926).

Similar transformations should accordingly be applied to all the thermodynamic functions calculated from  $\psi$ . At such concentrations, however, we know that the strict fundamental basis for the theory fails. In addition to this difficulty we must admit also that quantitative calculations based upon a highly specialised picture of shape, magnitude and internal properties of ions can hardly lead to results of much quantitative value. It is not surprising, therefore, that the ionic diameters fitting equation (44) are frequently of an improbable order of magnitude. Although it is noticeable that the above equation for  $\psi$  is, at sufficiently great dilution, compatible with the linear deviations from the ideal law as presented by equation (11).

### 5. Weak Electrolytes.

While the original theory of Arrhenius applies successfully only to simple solutions of ordinary weak acids and bases, the phenomena in more complicated cases (*e.g.*, when salts are added or when the weak electrolytes are ions themselves) have been satisfactorily accounted for on the basis of the modern theory of strong electrolytes.

As long ago as 1899 Arrhenius,<sup>39</sup> on the basis of catalytic experiments, concluded that addition of a neutral salt, such as NaCl, to a solution of a weak acid caused an increase in its dissociation. From the modern point of view this is easily understood as a result of the diminution of the activity coefficients of the ions, the activity coefficient of the undissociated molecules of the weak acid being practically unaffected. In such cases the ordinary mass action law is no longer applicable.

In the general case of an acid dissociating according to the scheme  $A \rightarrow B + H^+$  instead of the classical mass action expression:

$$\frac{c_B c_{H^+}}{c_A} = K_e$$

we have to write:

$$\frac{a_B a_{H^+}}{a_A} = K_a$$

*i.e.*, while  $K_e$  is a quantity that varies with the salt concentration,  $K_a$  is, by the definition of the activity conception, a true constant.

By introduction of the limiting law for the activity coefficients we obtain:

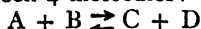
$$\log K_e = \log K_a - z_B \sqrt{\mu} \quad . \quad . \quad . \quad (45)$$

While for the dissociation constant of bases:

$$\log K_e = \log K_a + z_A \sqrt{\mu} \quad . \quad . \quad . \quad (46)$$

When A is of the type represented by acetic acid, introduction of  $a = f$  shows an increase in dissociation to take place on addition of salts like NaCl while for instance for  $A = NH_4^+$  there is no effect, and for  $A = Cr(H_2O)_6^{+++}$  a decrease in dissociation has to be expected.

In the equilibrium between 4 molecules:



the limiting equation is

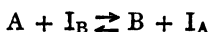
$$\log K_e = \log K_a - (z_C z_D - z_A z_B) \sqrt{\mu} \quad . \quad . \quad (47)$$

At higher concentrations according to the laws of  $f$  we have to expect linear deviations of  $\log K_e$  from the values given by the above equations.

<sup>39</sup> Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899).

Changes of  $K_e$  with changing  $\mu$  are available for experimental determinations in different ways.

By colorimetric methods applied for instance to indicator-buffer equilibrium:

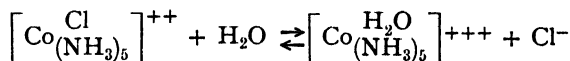


A and B being the acid and base in the buffer,  $I_A$  and  $I_B$  the acid and basic form of the indicator,<sup>40</sup> it is possible to measure the equilibrium displacement on addition of salts. Furthermore, by kinetic measurements, when one of the components in the equilibrium is catalytically active. The latter method has been used for semi-quantitative verification of the requirement of the theory in cases where hydrogen, hydroxyl or acetate and propionate ions function as catalysts.<sup>41</sup> For the dissociation of the chromic ion  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$  Brönsted and King recently found:

$$\log K_e = -3.90 - 2.0\sqrt{\mu} + 4.5\mu$$

at 15°, using for their determination of  $c_H^+$  the kinetic diazoacetic ester method. This is in conformity with theoretical equation (45) since  $z_B$  in this case is 2.

If the equilibrium is established sufficiently slowly, of course, analytical methods are available. For instance, the reaction studied in this way by



Lamb and Marden<sup>42</sup> shows the expected displacement on changing the ionic concentration.

By means of conductivity also it is possible with certain provisos to measure the partial dissociation as shown by Bjerrum<sup>6</sup> in his development of the theory of complete dissociation, and later by Schreiner.<sup>43</sup> In these investigations an empirical cube root expression for the activity coefficient was used.

In the study of the equilibrium between weak acids and bases also the electrometric method has often been applied.<sup>44</sup> The constant obtained most directly in this way is  $K_C$ , namely by comparing the hydrogen ion potential in the test solution with the potential in a solution of approximately the same concentration and nature and having a known hydrogen ion concentration. When eliminating the liquid junction potential and measuring against a constant normal electrode the method gives the important constant:

$$K_{\text{Acid}} = \frac{c_B}{c_A} \cdot a_{\text{H}^+} = K_a \frac{f_A}{f_B} \quad . \quad . \quad . \quad (48)$$

which is the most general and most adequate measure for the strength of an acid.  $K_{\text{Acid}}$  is called the acidity constant.

It is obvious from equation (48) that measuring  $a_{\text{H}^+}$  electrometrically, for instance in a buffer solution under various conditions, permits of the calculation of the ratio  $\frac{f_A}{f_B}$ . In this way, for instance, the Sørensen phos-

<sup>40</sup> Brönsted, *J. C. S.*, **119**, 574 (1921); *Rec. T. B.*, **42**, 718 (1923).

<sup>41</sup> Brönsted and Tetter, *J. physik. Chem.*, **28**, 579 (1924).

Brönsted and Petersen, *Z. physik. Chem.*, **108**, 185 (1924).

Brönsted and King, *J. Am. Chem. Soc.*, **47**, 2523 (1925).

<sup>42</sup> Lamb and Marden, *ibid.*, **33**, 1873 (1911).

<sup>43</sup> Schreiner, *Z. anorg. Chem.*, **115**, 181 (1921).

<sup>44</sup> See for instance, Schreiner, *Z. anorg. Chem.*, **122**, 201 (1922).

phate buffers were shown to conform satisfactorily to the modern theory. Further verification of the theory of buffer solutions has been published recently by Cohn.<sup>45</sup>

The present theory of weak electrolytes also applies of course to the solvent itself. Harned<sup>46</sup> recently studied the dissociation of water in the presence of salts from this point of view, verifying, for the region of small salt concentration, the expected increase in dissociation.

## 6. Concentrated Salt Solutions.

One of the most characteristic features of the behaviour of strong salt solutions is the fact, known for a long time and recently studied carefully by Harned and his co-workers,<sup>47</sup> that the activity coefficients, decreasing with increasing concentration in the dilute range, pass at higher concentrations through a minimum and thereafter increase rapidly. The assumption of hydration of the ions has presented itself as the immediate and most plausible explanation of this phenomena. In a solution of increasing salt concentration the hydration has a double effect. First to increase the salt concentration calculated as a mole fraction by removing the water molecules; then to liberate the free ions, the activity of which is under consideration, as a result of the increasing dehydrating effect of the salt solution. If hydration were the only factor to prevent a law of dilute solutions from holding true in the region of concentrated solution, it would be possible to calculate the degree of hydration from measurements of the deviation coefficients<sup>48</sup> and thus furnish an interpretation of the course of the activity coefficient. Since in concentrated solutions, however, the effect is certainly of much more complex character than the theory suggests, the hydration values calculated on this basis cannot be accepted as true values.

The original Debye-Hückel theory of dilute solutions was based upon the consideration of small  $\psi$ -potentials, disregarding the effect of a closer approach of ions and also of the change in dielectric constant with changing concentration, a treatment of the problem which is no longer permitted when the solution is concentrated. There have been attempts to extend it, by considering not only  $\frac{\psi\epsilon}{kT}$  but also the next members in the expansion of the hyperbolic *sine* function, (see sec. 4). The fundamental ideas of the Debye-Hückel theory, however, do not lend themselves to quantitative treatment on this basis. From a different point of view, Bjerrum<sup>49</sup> recently attacks the problem of stronger salt solutions by considering ions within a certain critical distance from one another as "associated," *i.e.*, as having no electric effect, calculating the number of such ion pairs by the Boltzmann principle and the thermodynamic mass action law. To the remaining "free" ions Bjerrum applies the Debye-Hückel theory. Even if this is strictly permissible only in dilute solution, this treatment would probably conform better to the actual conditions in salt solutions of higher concentration or of higher valence type; in fact it furnishes more

<sup>45</sup> Cohn, *J. Am. Chem. Soc.*, **49**, 173 (1927).

<sup>46</sup> Harned, *ibid.*, **47**, 930 (1925); **48**, 126 (1926).

<sup>47</sup> *Ibid.*, **44**, 2729 (1922); **47**, 676, 684, 689 (1925); **48**, 126, 326 (1926).

<sup>48</sup> Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

E. Schreiner, *ibid.*, **121**, 321 (1921); **135**, 333 (1924).

<sup>49</sup> Bjerrum, *Kgl. Danske. Vid. Selsk. Medd.*, **7**, No. 9 (1926).

plausible values for the ionic "size" than the extension of the Debye-Hückel theory to such regions when no regard is taken of higher terms.

On the other hand the complete mathematical solution of equation (22), as recently shown by LaMer and Grönwall,<sup>60</sup> appears to give perhaps still more plausible values of ionic sizes, without introducing a similar picture of ionic association.

The effect of strong salt concentration on the polarisation and dielectric constant of the solvent has recently been the subject of an investigation by E. Hückel.<sup>61</sup> He shows that when the solvent is more polarisable than the ions, in addition to the Coulomb forces, there arise repulsive forces between the ions which result in an increase of the activity coefficients eventually above unity. Furthermore change in the dielectric constant with changing salt concentration makes the self-potential of the ion, which was neglected in the Debye-Hückel theory for the case of dilute solution, appear as a significant quantity in the domain of concentrated solutions. Since the dielectric constant diminishes with increasing salt concentration this effect like that of hydration tends to increase the activity coefficient. This agrees qualitatively with the experimental facts. Quantitative calculations, based on the assumption of a linear variation of the dielectric constant with concentration, are rendered valueless by the fact that trustworthy information about the dielectric properties of salt solutions are lacking.

The few existing data<sup>52</sup> show a variation with concentration of quite a different order of magnitude than the ones fitting Hückel's calculations.

Scatchard<sup>18</sup> and Harned<sup>53</sup> found their measurements compatible with Hückel's theory. Güntelberg<sup>18</sup> also found the formula of Hückel to correspond excellently with his measurements on HCl-cells, but criticises the theory from the point of view that this agreement is present just as well in cases where the formula has no longer a physical meaning.

Quite recently Grönwall and LaMer<sup>64</sup> have submitted the Hückel theory to a careful criticism, and find results which are quite different from those of Hückel, basing their own arguments, however, on the same ideas of the predominating influence of a purely electrical effect.

To all these treatments of strong salt solutions the same objection applies, that the phenomena observed are certainly of much more complex nature than each theory assumes. When hydration, electric Debye-Hückel effects, ionic association, change in dielectric constant, etc. unite, as they certainly do, in influencing the behaviour of ions, any theory which can explain the observations on the basis of a few or one of these influences cannot possibly be trusted as a sound solution of the problem. It should not be overlooked that strong salt solutions exert a very remarkable effect also on molecules having no electrical net charge at all. This general effect is certainly a factor of great consequence, but has not been sufficiently recognised in any of the theories of strong salt solutions hitherto advanced.

Only in one sense are concentrated salt solutions characterised by great simplicity. If a strong solution acts as a solvent for other salts, present in concentrations small compared with that of the solvent salt, then variations in this solute system keeping the medium or solvent salt unchanged will not, as in the case of a pure water solution, invalidate the ordinary gas laws and

<sup>60</sup> LaMer and Grönwall: unpublished.

<sup>61</sup> Hückel, *Physik. Z.*, **26**, 93 (1926).

<sup>52</sup> Walden, Ulich, and Werner, *Z. physik. Chem.*, **116**, 261 (1925).

<sup>53</sup> Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

<sup>64</sup> Grönwall and LaMer, unpublished; preliminary note, *Science*, **64**, 122 (1926).

make the mass action law inapplicable. It has been shown<sup>55</sup> that the Nernst formula for electromotive force, the solubility product and mass action law in the case of a complicated ionic equilibrium are applicable in their classical form to such concentrated salt solutions, the reason for this simplicity being the practical constancy of the activity coefficients in the practically constant medium. Utilisation of these results would mean in many cases a great simplification in problems pertaining to electrolytic solutions.

## 7. Non-Aqueous Solutions.

In solvent media with smaller dielectric constants than water the increased electric forces will cause larger deviations from the ideal laws of solutions. We must expect the limit for the application of the Debye-Hückel theory for such solutions to lie in a still more dilute range than for water. The tendency of ions to associate, which is of course increasing with increasing charge, and under equal conditions with decreasing size, will make itself more marked for such solvents. Substances which are practically strong electrolytes in water may prove to be weak or incompletely dissociating substances in non-aqueous solvents.

The electrometric measurements of Harned and Fleysher<sup>56</sup> and Lucasse,<sup>57</sup> and the calculations of A. A. Noyes and Baxter,<sup>58</sup> show a fair approximation to the theoretical Debye-Hückel slope, and verify the effect of the dielectric constant. Schreiner and Frivold<sup>59</sup> by freezing-point measurements of several salts in cyclohexanol (with a dielectric constant of 15) also found a good agreement with the theory.

In these cases, in spite of the low dielectric constant, the theory of complete dissociation seems to hold fairly well. Brönsted and Delbanco<sup>60</sup> determined the effect of  $\text{KNO}_3$  upon the solubility of flavo-cobaltic chloride

in furfural finding as limiting slope:  $\frac{d \log f}{d \sqrt{m}} = 2.2$  instead of the theoretical value 1.43, calculated from  $D = 40$ . Deviations in the same direction are found by Kraus<sup>61</sup> by solubility measurements in isopropyl alcohol and acetone as solvents.

The ratio of the dissociation constants for acids passing from one solvent to another seems to be relatively constant for acids of similar structure.<sup>62</sup> For water and alcohol as solvents the ratio seems to be about  $10^6$ . While a substance like  $\text{HCl}$  is practically completely dissociated in dilute aqueous solution, this is no longer the case in alcohol. Schreiner<sup>63</sup> from kinetic measurements calculates the dissociation constant  $K = 10^{-2}$  for an ethyl alcohol solution, and so concludes that the constant for water solution is about  $10^4$ . According to Ebert<sup>64</sup> the dissociation constant for  $\text{HBr}$  is 100

<sup>55</sup> Brönsted *Vid. Selsk. Skr.* (7), 12, No. 6 (1915); *Medd. Vet. Nob.* 5, No. 25 (1919); *Vid. Selsk. Medd.*, 3, No. 9 (1920); *Z. physik. Chem.*, 98, 239 (1921).

Brönsted and Petersen, *ibid.*, 103, 307 (1922).

For further experimental evidence in favour of this conclusion see Lewis and Sargent, *J. Am. Chem. Soc.*, 31, 355 (1909).

<sup>56</sup> Harned and Fleysher, *ibid.*, 47, 82 (1925).

<sup>57</sup> Lucasse, *ibid.*, 48, 626 (1926).

<sup>58</sup> A. A. Noyes and Baxter, *ibid.* 47, 2122 (1925).

<sup>59</sup> Schreiner and Frivold, *Z. physik. Chem.*, 124, 1 (1926).

<sup>60</sup> Brönsted and Delbanco, unpublished.

<sup>61</sup> Kraus, unpublished.

<sup>62</sup> Goldschmidt, *Z. physik. Chem.*, 99, 116 (1921).

Larsson, *Dissertation*, Lund, 1924.

<sup>63</sup> Schreiner, *Z. physik. Chem.*, 111, 419 (1924).

<sup>64</sup> Ebert, *Naturwiss.*, 13, 393 (1925).

times that for HCl, in spite of the fact that they give by ordinary methods the same degree of dissociation. This of course is quite analogous to very weak acids giving the same dissociation as measured by the freezing-point method even though the strength be very different. This exemplifies the obliterating effect of strongly dissociating solvents upon individual characteristics as emphasised by Hantzsch.<sup>65</sup>

In the case of acids and bases the dissociation phenomena depend largely on the acidic and basic properties of the solvents.

It is possible to look upon the equilibrium phenomena in different solvents as governed by the absolute activity of the constituents. The electric contribution to the activity changes from a very simplified picture of a molecule<sup>66</sup> is given by

$$\ln f = \frac{z^2 \epsilon^2}{2rkDT} \quad . \quad . \quad . \quad . \quad . \quad (49)$$

$r$  being the radius of the molecule considered and the rest of the notation being the same as in Section 4. For instance for the acidity of the same acid in two different solvents this equation gives:

$$\ln \frac{K_{\text{Acid (1)}}}{K_{\text{Acid (2)}}} = \frac{\epsilon^2}{2rkT} \left( \frac{1}{D_1} - \frac{1}{D_2} \right) (2z_B + 1) \quad . \quad . \quad . \quad (50)$$

$z_B$  being the valence of the corresponding base. This formula conforms qualitatively with the experiments for acids of various charge type in various solvents but, as expected, shows no quantitative agreement<sup>67</sup> since other effects than those purely electrical are present. The applicability of formula (49) to the calculation of the activity coefficients of several strong electrolytes in water and alcohol mixtures<sup>68</sup> can therefore not be looked upon as a proof of its applicability in general.

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<sup>65</sup> Hantzsch, *Z. Electrochem.*, **29**, 221 (1923).

<sup>66</sup> See Born, *Z. Physik.*, **1**, 45 (1920).

<sup>67</sup> Brönsted, *Festschrift, Københavns Universitet* (1926).

<sup>68</sup> Scatchard, *J. Am. Chem. Soc.*, **47**, 2098 (1925); *Chemical Reviews*, **3**, 383, (1926).

## GENERAL DISCUSSION

**Professor Bjerrum** said that as pointed out by Professor Brönsted it certainly represented great progress to introduce in the square root term of the activity coefficient the conception of ionic strength  $\mu = \sum z_i^2 c_i$ .

So far as he was aware, however, there were no data making it probable that it would be equally useful to introduce the ionic strength in the linear term of the activity coefficient. It therefore seemed to be a little dangerous to write

$$- \ln f = Az^2 \sqrt{\mu} + B\mu.$$

An essential part of the linear term seemed to be additive and might be written  $\sum B_i c_i$  or  $\sum B_i L_i^{\circ} z_i^2 c_i$ , where  $c_i$  was the molar concentration and  $z_i$  the valence of the  $i$ th kind of ions and  $B_i$  (or  $B_i^{\circ}$ ) a constant determined by

the nature of the ion whose activity coefficient was considered and that of the ion of the  $i$ th species.

Writing the linear term in the form  $B\mu$  there followed :

$$B = \sum B_i \frac{c_i}{\mu} = \sum B_i L_i \frac{z_i^2 c_i}{\mu}.$$

Thus  $B$  was a complicated constant varying both with the nature and the concentration ratios of all the ions present.

**Mr. W. F. K. Wynne-Jones** said that in the extension of the Debye-Hückel theory to weak electrolytes, it had been found that the treatment suggested by Davies<sup>1</sup> was applicable not only to aqueous solutions but also to non-aqueous solutions where the deviations from the Ostwald Dilution Law were considerable. While on the empirical side, this treatment seemed quite satisfactory, he was not certain of the theoretical assumptions involved and he asked Mr. Fowler whether analysis would reveal any uncertainty in this extension.

**Dr. Onsager** said that in such cases it would be best to apply the mass-action law even if no sharply defined formation of molecules occurred, but only "association" in the sense of Professor Bjerrum.

(*Added later.*) Though the degree of dissociation was not sharply defined of itself, it might be convenient to settle a suitable arbitrary definition, such as suggested by Professor Bjerrum. It was true, that even if this definition be given, mathematical methods were not sufficiently advanced to tell exactly how a "completely dissociated" electrolyte would behave. However, in some cases it was possible to find electrolytes which might be supposed to fit this idea of "complete dissociation" fairly well, such as certain chlorides in aqueous solution, and these might be used as prototypes for comparison with other electrolytes of the same type. Actually, univalent binary electrolytes, for example, required a series of prototypes, because the decrease in conductance depended upon the limiting conductance.

He would expect correlation between the results found from conductance and from activity measurements, and the method might perhaps make it possible to characterise the chief individual properties of an electrolyte by one single constant, or by a few constants (see Professor Brönsted's principle of specific interaction, p. 420).

The conductance and activity curves of the "prototype" should of course be extrapolated so as to fit the limiting square root formula asymptotically in great dilutions. For electrolytes which were so weak that the mutual effects of inter-ionic forces only involved minor corrections to the mass-action law, these corrections might often be computed with sufficient accuracy from the limiting formula alone.<sup>2</sup>

**Professor Bjerrum** said that in the foregoing discussions the expression "associated ions" had several times been used and reference had been made to a paper of the speaker's on associated ions. In order to avoid misunderstanding he wished explicitly to state that the expression "associated ions" was used by him only for ions which, without combining chemically, were so near each other that the work necessary to separate their electric charges was four times greater than the mean kinetic energy per degree of freedom  $\left(4 \frac{kT}{2}\right)$ . The distinction between free and associated ions was not a chemical one, but only a mathematical device

<sup>1</sup> *J. physical Chem.*, **29**, 977 (1925).

<sup>2</sup> *Kgl. Danske Vidensk. Selsk.*, 1926.

making possible an approximate calculation of the effect of interionic forces under conditions where the approximation of Debye and Hückel could not be used.

**Mr. Fowler** said that it should be borne in mind in discussing association of ions that so long as the ions might be regarded as of given undeformed structure association could at most mean the juxtaposition of two ions of opposite sign with insufficient energy to escape from each other's electric fields. In such conditions the energy of the relative motion would strictly be quantised, but for massive ions the consequent deviations from classical distribution laws would be negligible. Owing to the sizes of the ions they could never reach very large negative energies as could free electrons. That being so, Boltzmann's equation as usually employed automatically took *complete* account of associations of ions in that sense. It had been obtained by prior integration over all kinetic energies of the relative motion from zero upwards.

When one applied similar considerations to matter in the state in which it must exist within a star—an assemblage of free electrons and atomic ions of large positive charge, one could no longer proceed in that simple way. It was necessary to take explicit account of quantum conditions for bound electrons. The electrons must therefore be divided into free and bound and a modification of Boltzmann's equation was necessary.

**Professor Brönsted** said that Professor Bjerrum had criticised equation (11) in his paper from the point of view of the term B not giving a general representation of the linear salt effect. However equation (11) was claimed to hold only for the case of a "constant type of the solvent solution" which actually meant that the expression held true if the concentration change was due to the simple effect of dilution. For this case Equation (11) was just as exact as (8) and (9). There was of course no difficulty in generalising the expression still more by introducing for B the sums of individual effects  $\Sigma B_i m_i$ , or  $\Sigma B_i c_i$  or  $\Sigma B_i \mu_i$ . In most practical cases (11), however, was directly applicable, this form of the equation having the great advantage of permitting a simple graphical treatment.

## STRONG ELECTROLYTES IN RELATION TO STATISTICAL THEORY, IN PARTICULAR THE PHASE INTEGRAL OF GIBBS.

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### 1. Introduction.

The sole accepted and sufficient principle which yields the whole kinetic theory of matter as hitherto developed is that the equilibrium state of any assembly is fully determined by the properties of the phase integral of Gibbs. This principle need not be derived in Gibbs' manner and may be modified in detail by quantum requirements, perhaps even fundamentally for very dense matter by the new mechanics, but its essential nature remains unaffected. In view of its complete generality it seems desirable to examine the relationship to it of the theory of strong electrolytes

proposed by Debye and Hückel.<sup>1</sup> Any theory such as their's can only be a short cut to the evaluation of Gibbs' phase integral in particular complicated cases, in which a direct evaluation such as that attempted by Milner<sup>2</sup> is almost prohibitively difficult. Unless in fact such a theory can be shown to be such a short cut, it can be of no *quantitative* value in applications. It is not immediately obvious that the beautiful short cut proposed by Debye and Hückel does conform to this requirement and so evaluate quantitatively the contribution of the ionic charges to the characteristic function or other thermodynamic potential of the assembly. The object of this article is to establish conditions under which this short cut is legitimate.

In the problem in hand it is unnecessary to consider refinements required by the quantum theory or the new mechanics. If  $W$  is the complete potential energy of the assembly as a function of its configuration in space, and independent of the momenta of its particles,<sup>3</sup> then the phase integral, or partition function for distribution of potential energy, which controls also completely the distribution of the component systems in configuration, is

$$B(T) = \int \dots \int_{(V)} e^{-W/kT} \Pi_{\kappa}(d\omega_{\kappa})^{N_{\kappa}} \dots \quad (1)$$

The integral is of course an integral over the whole configuration space and  $\Pi_{\kappa}(d\omega_{\kappa})^{N_{\kappa}}$  is merely a shortened form of

$$\prod_{r=1}^{N_{\alpha}} (dx_{\alpha} dy_{\alpha} dz_{\alpha})_r \prod_{r=1}^{N_{\beta}} (dx_{\beta} dy_{\beta} dz_{\beta})_r \dots$$

extended to each type of system present in the assembly to the number of  $N_{\alpha}, N_{\beta} \dots$ , respectively. Planck's characteristic function  $\Psi$ , besides contributions from the translational kinetic and internal energies of the systems, contains only a term  $k \log B(T)$ , where  $k$  is Boltzmann's constant. This is the sole contribution to the characteristic function made by the potential energy and the distribution in configuration.

If  $W$  is zero or effectively zero then obviously

$$B(T) = V^{z_{\kappa} N_{\kappa}} \dots \quad (2)$$

If  $W \neq 0$  evaluation of  $B(T)$  becomes at once extremely difficult. When  $W$  is made up entirely of contributions of short range forces between each pair (etc.) of molecules, step by step methods of approximation to  $B(T)$  have been current since Boltzmann. This case does not directly concern us here. When an important part of  $W$  arises from forces obeying the inverse square law, such a method seems almost impossible and we are driven back on less direct methods of computing  $B(T)$  through a study of molecular distribution laws. Our object is to show that the method of Debye and Hückel reduces to such a method of calculating  $B(T)$ , and is therefore a valid section of statistical theory.

## 2. Molecular Distribution Laws.

When there are no external fields or long range forces (and this allows of electrostatic forces of zero space charge) the ordinary uniform space

<sup>1</sup> Debye and Hückel, *Physik. Z.*, **24**, 185, 305 (1923); Debye, *ibid.*, **25**, 97 (1924).

<sup>2</sup> Milner, *Phil. Mag.*, **23**, 551 (1912); **25**, 743 (1913). Milner worked on the virial, but the principle is the same.

<sup>3</sup> An exposition of the detailed statistical basis of this article is given by Fowler, *Proc. Camb. Phil. Soc.*, **22**, 861 (1925). This paper also contains a first attempt at a discussion of the theory of Debye and Hückel, which is the origin of the revised form given here.

distribution law can be deduced at once for each type of system from the properties of  $B(T)$ . For the frequency ratio for the presence of a selected system in a given volume element  $\delta V$  is  $\delta B(T)/B(T)$ , where

$$\delta B(T) = \int_{\delta V} d\omega_a \int \dots \int_{(V)} e^{-W/kT} \Pi'_\kappa(d\omega_\kappa)^{N_\kappa} \quad (3)$$

just one  $d\omega_a$  integration over  $V$  being omitted. This is noted by the prime to  $\Pi_\kappa$ .  $W$  can here depend only on the *relative* co-ordinates of the various systems and

$$\int \dots \int_{(V)} e^{-W/kT} \Pi'_\kappa(d\omega_\kappa)^{N_\kappa}$$

must reduce to a constant  $Q$  independent of the co-ordinates of the selected  $a$ . Hence obviously

$$\delta B(T) = Q\delta V, \quad B(T) = QV. \quad (4)$$

The frequency ratio is therefore  $\delta V/V$  and since there are  $N_a$  such systems the average number  $\bar{a}_a$  present in equilibrium in  $\delta V$  is given by the familiar formula,

$$\bar{a}_a = N_a \delta V/V, \quad (5)$$

which is thus established for a gas of any degree of imperfection, or in fact for any fluid.

By the same argument the average number  $\bar{a}_{\alpha\beta}$  of  $(\alpha, \beta)$ -pairs simultaneously present in selected volume elements  $\delta V_\alpha$  and  $\delta V_\beta$  must be given by

$$\bar{a}_{\alpha\beta} = \frac{N_\alpha N_\beta}{B(T)} \int_{\delta V_\alpha} \int_{\delta V_\beta} d\omega_\alpha d\omega_\beta \int \dots \int_{(V)} e^{-W/kT} \Pi''_\kappa(d\omega_\kappa)^{N_\kappa} \quad (6)$$

In the same absence of long range forces the integral in (6) must be a function only of the relative co-ordinates of the selected  $\alpha$  and  $\beta$ . If  $\delta V_\alpha$  and  $\delta V_\beta$  are small on the molecular scale, we can treat these relative co-ordinates as constant over  $\delta V_\alpha$  and  $\delta V_\beta$  and write

$$\bar{a}_{\alpha\beta} = \frac{N_\alpha N_\beta}{B(T)} \frac{\delta V_\alpha \delta V_\beta}{V^2} Q e^{-W_{\alpha\beta}/kT} \quad (7)$$

where  $W_{\alpha\beta}$  is so defined that  $W_{\alpha\beta} \rightarrow 0$  at infinite separation and  $Q$  is a constant.  $W_{\alpha\beta}$ , the average potential energy of  $\beta$  in the field of  $\alpha$ , depends in general on the average positions of other molecules and is therefore a function of the temperature. Again

$$B(T) = \int_V \int_V Q e^{-W_{\alpha\beta}/kT} d\omega_\alpha d\omega_\beta = QV^2 \quad (8)$$

approximately, when  $W_{\alpha\beta} \rightarrow 0$  rapidly (as in fact it does) for large separations. Thus

$$\bar{a}_{\alpha\beta} = N_\alpha N_\beta e^{-W_{\alpha\beta}/kT} \delta V_\alpha \delta V_\beta / V^2 \quad (9)$$

and the average number of  $\beta$ 's in a selected  $\delta V_\beta$  relative to any  $\alpha$  anywhere in the assembly is

$$N_\beta e^{-W_{\alpha\beta}/kT} \delta V_\beta / V. \quad (10)$$

Formulae (9) and (10) are commonly known as Boltzmann's Theorem. They are true of course for any sort of assembly whatever, but *subject to the proper definition of  $W_{\alpha\beta}$  given above*, which really reduces them to

definitions of  $W_{\alpha\beta}$ . Great care is necessary before asserting other properties of  $W_{\alpha\beta}$ .

The foregoing section is merely one example of the general theorem that if  $X$  is any function of the co-ordinates of the molecules and

$$\bar{X}B(T) = \int \cdot \cdot \cdot \int_{(V)} e^{-W/kT} X \Pi_{\alpha}(d\omega_{\kappa})^{N_{\kappa}} \quad (11)$$

then this average value  $\bar{X}$  is the value of  $X$  presented or possessed by the assembly in equilibrium.

### 3. Properties of $W_{\alpha\beta}$ .

If we differentiate the equation defining  $W_{\alpha\beta}$  contained in (6) and (7) we find

$$Qe^{-W_{\alpha\beta}/kT} \frac{\partial W_{\alpha\beta}}{\partial x_{\beta}} = \int \cdot \cdot \cdot \int_{(V)} \frac{\partial W}{\partial x_{\beta}} e^{-W/kT} \Pi_{\kappa}''(d\omega_{\kappa})^{N_{\kappa}}, \quad (12)$$

which can be reduced to

$$\frac{\partial W_{\alpha\beta}}{\partial x_{\beta}} \int \cdot \cdot \cdot \int_{(V)} e^{-W/kT} \Pi_{\kappa}''(d\omega_{\kappa})^{N_{\kappa}} = \int \cdot \cdot \cdot \int_{(V)} \frac{\partial W}{\partial x_{\beta}} e^{-W/kT} \Pi_{\kappa}''(d\omega_{\kappa})^{N_{\kappa}} \quad (13)$$

There are two similar equations. Since  $W$  is the complete potential energy of the configuration,  $-\partial W/\partial x_{\beta}$  etc. are the force components acting on the selected  $\beta$  in the selected position relative to the selected  $\alpha$ , or *vice versa*. The definition of  $W_{\alpha\beta}$  is therefore such that its partial derivatives are the average partial derivatives of  $W$ , *i.e.*

$$\frac{\partial W_{\alpha\beta}}{\partial x_{\beta}} = \frac{\partial \bar{W}}{\partial x_{\beta}} \quad (14)$$

Again, if we differentiate (13) with respect to  $x_{\beta}$  and add the two similar equations we find

$$\begin{aligned} & \left\{ \nabla_{\beta}^2 W_{\alpha\beta} - \frac{1}{kT} \Sigma \left( \frac{\partial W_{\alpha\beta}}{\partial x_{\beta}} \right)^2 \right\} \int \cdot \cdot \cdot \int_{(V)} e^{-W/kT} \Pi_{\kappa}''(d\omega_{\kappa})^{N_{\kappa}} \\ &= \int \cdot \cdot \cdot \int_{(V)} \left\{ \nabla_{\beta}^2 W - \frac{1}{kT} \Sigma \left( \frac{\partial W}{\partial x_{\beta}} \right)^2 \right\} e^{-W/kT} \Pi_{\kappa}''(d\omega_{\kappa})^{N_{\kappa}}. \end{aligned} \quad (15)$$

Let us now suppose that  $W$  is derived entirely from electrostatic forces. This is probably true of matter in the state in which it must exist inside many stars. The adaptation necessary for application to solutions of strong electrolytes is considered in § 4. On this supposition  $W$  will obey Poisson's equation,

$$\nabla_{\beta}^2 W = -4\pi\rho z_{\beta}\epsilon, \quad (16)$$

where  $\rho$  is the smoothed local space charge of the given configuration and  $z_{\beta}\epsilon$  is the charge on the  $\beta$  ion,  $\epsilon$  being the (positive) electronic charge. Therefore

$$\int \cdot \cdot \cdot \int_{(V)} \nabla_{\beta}^2 W e^{-W/kT} \Pi_{\kappa}''(d\omega_{\kappa})^{N_{\kappa}} = -4\pi\bar{\rho}z_{\beta}\epsilon \int \cdot \cdot \cdot \int_{(V)} e^{-W/kT} \Pi_{\kappa}''(d\omega_{\kappa})^{N_{\kappa}},$$

where  $\bar{\rho}$  is the smoothed local space charge averaged for all configurations. We may therefore write (15) in the form:

$$\nabla_{\beta}^2 W_{\alpha\beta} + 4\pi\bar{\rho}z_{\beta}\epsilon = \frac{1}{kT} \left[ \Sigma \left( \frac{\partial W_{\alpha\beta}}{\partial x_{\beta}} \right)^2 - \Sigma \left( \frac{\partial \bar{W}}{\partial x_{\beta}} \right)^2 \right]. \quad (17)$$

The terms on the right are the mean square fluctuation of the resultant electric force on  $\beta$  near the specified  $\alpha$  divided by  $(-kT)$ . Criticism of this use of (16) is possible, but cannot I think be sustained, so that, within the limits imposed, (17) should be of general validity.

#### 4. Adaptations to Solutions of Strong Electrolytes.

In discussing solutions of electrolytes, we must remember firstly that the electrostatic forces form only a minor part of  $W$ , and secondly that it is not our object to calculate the whole of  $B(T)$  in terms of intermolecular forces, but only the *correction* to  $B(T)$  and the *correction* to the distribution laws due to the electrostatic forces. To adapt the work of § 3 we write  $W = W_s + W_l$ , where the suffixes indicate energies arising from forces of short and long ranges respectively, the latter being electrostatic. Equation (14) then reads

$$\frac{\partial W_{\alpha\beta}}{\partial x_\beta} = \frac{\partial W_s}{\partial x_\beta} + \frac{\partial W_l}{\partial x_\beta} \quad (18)$$

In the absence of large scale long range fields of force and, at a distance apart of the  $\alpha$  and  $\beta$  sufficient to ensure that they do not actually get in each other's way, we shall expect to have

$$\int \cdot \cdot \cdot \int_{(V)} \frac{\partial W_s}{\partial x_\beta} e^{-W/kT} \Pi_\kappa''(d\omega_\kappa)^{N_\kappa} = 0, \quad \frac{\partial W_s}{\partial x_\beta} = 0. \quad (19)^4$$

We may then properly assert for a solution of a strong electrolyte that in place of (13)

$$\frac{\partial W_{\alpha\beta}}{\partial x_\beta} \int \cdot \cdot \cdot \int_{(V)} e^{-W/kT} \Pi_\kappa''(d\omega_\kappa)^{N_\kappa} = \int \cdot \cdot \cdot \int_{(V)} \frac{\partial W_l}{\partial x_\beta} e^{-W/kT} \Pi_\kappa''(d\omega_\kappa)^{N_\kappa} \quad (20)$$

Equation (20) however is valid only for separations of the  $\alpha$  and  $\beta$  above a certain limit. For separations below a certain limit (the mean diameter of the  $\alpha$  and  $\beta$ ) there can never be a  $\beta$ , and there will also be a transition region between the two limits, of more or less importance, in which van der Waal's attractive forces and perhaps the pressure effects mentioned in the footnote play a part. Proceeding on from (20) we can replace (15) by

$$\left\{ \nabla_\beta^2 W_{\alpha\beta} - \frac{1}{kT} \Sigma \left( \frac{\partial W_{\alpha\beta}}{\partial x_\beta} \right)^2 \right\} \int \cdot \cdot \cdot \int_{(V)} e^{-W/kT} \Pi_\kappa''(d\omega_\kappa)^{N_\kappa} \\ = \int \cdot \cdot \cdot \int_{(V)} \left\{ \nabla_\beta^2 W_l - \frac{1}{kT} \Sigma \frac{\partial W_l}{\partial x_\beta} \left( \frac{\partial W_s}{\partial x_\beta} + \frac{\partial W_l}{\partial x_\beta} \right) \right\} e^{-W/kT} \Pi_\kappa''(d\omega_\kappa)^{N_\kappa}. \quad (21)$$

It seems reasonable to expect further that

$$\frac{\partial W_l}{\partial x_\beta} \frac{\partial W_s}{\partial x_\beta} = 0,$$

or at least negligible. Besides the pressure effect there is little correlation between long and short range forces during the averaging. Equation (15) therefore stands, with  $W_l$  instead of  $W$  on its right-hand side in the term  $\{ \cdot \cdot \cdot \}$ , under suitable limitations.

<sup>4</sup> This is perhaps not quite so certain as one is tempted to think at first. Zwicky, *Physik. Z.*, **27**, 271, (1926), has shown that each ion in a water-solution is a centre of greatly enhanced pressure due to the attraction of the inhomogeneous field of the ion for the water dipoles. In equilibrium the short range forces between the water molecules will balance this attractive effect. It is therefore likely that they will also exert a non-zero resultant force on the  $\beta$  ions. This pressure has an important effect on the specific heat of the solution, but from a rough estimate of relative magnitudes, I think it is usually negligible in (18), and that (19) is a valid approximation.

The charged bodies are now in a dense medium, and the obvious argument in applying Poisson's equation is to say that on the average the medium has a dielectric constant  $D$  equal to that of the medium in bulk for external electric fields—for dilute solutions  $D$  should then be the bulk constant for the pure solvent. Then

$$\nabla_{\beta}^2 W_i = -4\pi\rho z_{\beta}\epsilon/D \quad . \quad . \quad . \quad (22)$$

This argument is undeniably unsatisfactory. The main part of  $D$  arises from the average orientation of the water dipoles by the field of the ions. In obtaining (22) we have therefore used an illegitimate averaging process by working the complete averaging implied in  $B(T)$  in separate stages. The result may be right and cannot be in error by any large numerical factor, but a more extended examination is desirable. It will be interesting but doubtless difficult. Accepting (22) with the normal value of  $D$  we find in place of (17),

$$\nabla_{\beta}^2 W_{\alpha\beta} + \frac{4\pi\bar{\rho}z_{\beta}\epsilon}{D} = \frac{1}{kT} \left[ \Sigma \left( \frac{\partial W_{\alpha\beta}}{\partial x_{\beta}} \right)^2 - \Sigma \left( \frac{\partial W_i}{\partial x_{\beta}} \right)^2 \right] \quad . \quad (23)$$

It is not difficult to specify a little more closely the type of approximation made in (23). In the first place we have assumed that  $D$  is spatially constant near the  $\alpha$  ion, but it is quite possible that this is incorrect and that it may really decrease from a normal value at large separation as the  $\alpha$  ion is approached. Secondly we have as it were replaced  $(\rho/D)$  by  $\bar{\rho}/D$ .

We have now to consider if and when the fluctuation term in (23) can be neglected. The volume elements near any one ion to which our arguments have to be applied are small on the molecular scale and fluctuation terms may not be ignorable automatically as in ordinary statistical problems. A fluctuation term may be comparable with the average value of the term itself. It is therefore impossible to assert that the right-hand side is small compared with

$$\frac{1}{kT} \Sigma \left( \frac{\partial W_{\alpha\beta}}{\partial x_{\beta}} \right)^2 \quad . \quad . \quad . \quad (24)$$

The utmost that it is *safe* to conclude here is that the fluctuation is not of greater order than (24) and that Poisson's equation,

$$\nabla_{\beta}^2 W_{\alpha\beta} + \frac{4\pi\bar{\rho}z_{\beta}\epsilon}{D} = 0 \quad . \quad . \quad . \quad (25)$$

may be used so long as (24) is small compared with terms retained.

Any non-fluctuating part of  $W_{\alpha\beta}$  may be removed before applying this test for the validity of (25).

At present the validity of (25) must be verified *a posteriori* by a study of the order of (24) after (25) has been solved.

### 5. Validity of the Theory of Debye and Hückel for Dilute Solutions.

By virtue of (10) the  $\bar{\rho}$  in (25) has the value,

$$\bar{\rho} = \epsilon \Sigma_{\gamma} z_{\gamma} \frac{N_{\gamma}}{V} e^{-W_{\alpha\gamma}/kT}, \quad . \quad . \quad . \quad (26)$$

and we therefore find for  $W_{\alpha\beta}$  the equation,

$$\nabla_{\beta}^2 W_{\alpha\beta} = - \frac{4\pi\epsilon^2 z_{\beta}}{D} \Sigma_{\gamma} z_{\gamma} \frac{N_{\gamma}}{V} e^{-W_{\alpha\gamma}/kT}. \quad . \quad . \quad (27)$$

For the sake of statistical theory we have so far worked in energy, but it is of course more convenient to introduce the electrostatic potential  $\psi_a$  round the  $a$  ion by the equation  $W_{a\beta} = e z_\beta \psi_a$ . Then since  $\psi_a$  is spherically symmetrical,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi_a}{\partial r} \right) = - \frac{4\pi e}{D} \cdot \frac{\sum_\gamma z_\gamma N_\gamma}{V} e^{-z_\gamma e \psi_a / kT} \quad (28)$$

From this, as we all know, Debye and Hückel derive the result that

$$\psi_a = \frac{z_a e}{D} \frac{1}{r} e^{-\kappa r}, \quad \kappa^2 = \frac{4\pi e^2}{D kT} \sum_\gamma z_\gamma^2 \frac{N_\gamma}{V} \quad (29)$$

which is valid so long as (i)  $\kappa \sigma$  is small, where  $\sigma$  is of the order of the ionic diameter and (ii)  $z_\gamma e a_\kappa / kT$  is small for all values of  $r$  that matter—conditions which are satisfied in any fairly dilute solution of ions not too small. The average potential at the centre of an  $a$  ion is then

$$- \frac{\kappa z_a e}{D} \quad (30)$$

We have now to justify the neglect of the fluctuation term in (23). According to (29)

$$W_{a\beta} = \frac{z_a z_\beta e^2}{D} \frac{1}{r} e^{-\kappa r},$$

but of this  $z_a z_\beta e^2 / Dr$  is non-fluctuating, being due to the field of the  $a$  ion itself. The fluctuating residue is

$$W_{a\beta}' = \frac{z_a z_\beta e^2}{D} \frac{1}{r} (e^{-\kappa r} - 1) \quad (31)$$

and we must examine the relative orders of  $(\partial W_{a\beta}' / \partial r)^2 / kT$  and terms retained in (25) such as  $2(\partial W_{a\beta}' / \partial r) / r$ . Any other term would do. We find a ratio,

$$\frac{z_a z_\beta e^2 \kappa}{2D kT} \left[ \frac{1 - (1 + \kappa r) e^{-\kappa r}}{\kappa r} \right].$$

Since, for all positive  $x$ ,  $e^x \leq 1 + x + x e^x$ , it follows that the term in [ ] never exceeds unity, and the fluctuation term may be neglected if

$$\frac{z_a z_\beta e^2 \kappa}{2D kT}$$

is small. This is the same as  $W_{a\beta}' / kT$  small.

We conclude that there is a region in which the procedure of Debye and Hückel should be quantitatively correct (except perhaps for an error in  $D$  namely that in which  $W_{a\beta}' / kT$  is small), but that it is doubtful if it is worth while attempting to develop a solution of (28) in which higher powers of  $W_{a\beta}' / kT$  than the first are retained. This does not imply that it is worthless to attempt to include accurately the effect of the larger non-fluctuating part of  $\psi_a$ . The simple solution (29) was obtained on the assumption  $W_{a\beta} / kT$  small which may be more restrictive than  $W_{a\beta}' / kT$  small.

## 6. Calculation of $\Psi$ , the Characteristic Function.

Suppose that all the force centres contributing to  $W$  are gradually built up from zero by differential additions, *the assembly being all the time at constant temperature and at each stage in the equilibrium state corresponding*

to the force centres already present. This is an ideal process requiring the treatment of individual molecules, but none the less a conceivable reversible isothermal process in the thermodynamic sense, and the work done on the assembly in the process must on general thermodynamic principles be the increase in  $A (= U - ST)$ , the work function due to the establishment of the intermolecular fields. This important fact is by no means novel, but hardly sufficiently familiar. A direct statistical proof may be given as follows.

Suppose that every intermolecular energy term is at a fraction  $\sigma$  of its final value. Then the partition function  $B_\sigma(T)$  for the potential energy is given by

$$B_\sigma(T) = \int \dots \int_{(v)} e^{-\sigma W/kT} \Pi_\kappa(d\omega_\kappa)^{N_\kappa}, \quad (32)$$

and the average value of the potential energy in equilibrium by

$$kT^2 \frac{\partial}{\partial T} \log B_\sigma(T) = \frac{\sigma}{B_\sigma(T)} \int \dots \int_{(v)} W e^{-\sigma W/kT} \Pi_\kappa(d\omega_\kappa)^{N_\kappa}. \quad (33)$$

Keeping the distribution laws unaltered, but increasing each energy term from  $\sigma$  to  $\sigma + d\sigma$  increases the potential energy of the assembly by

$$\frac{d\sigma}{B_\sigma(T)} \int \dots \int_{(v)} W e^{-\sigma W/kT} \Pi_\kappa(d\omega_\kappa)^{N_\kappa}. \quad (34)$$

This increase of energy must therefore be the work necessary to strengthen the intermolecular energies from a fraction  $\sigma$  to a fraction  $\sigma + d\sigma$  of their final values. The total work required to build up the final force system by a reversible isothermal process is therefore given by integrating (34) with respect to  $\sigma$  from 0 to 1, obtaining

$$- kT \int_0^1 \frac{d}{d\sigma} \left\{ \log B_\sigma(T) \right\} d\sigma,$$

or

$$- kT \log \{ B(T)/V^{\sum \kappa N_\kappa} \}.$$

But this expression is just  $(-T)$  times the increase in  $\Psi$  due to the establishment of the intermolecular fields and  $-T\Psi = A$ .

A slight modification of this theorem is required here. We have in general,

$$B(T) = \int \dots \int_{(v)} e^{-(W_s + W_l)/kT} \Pi_\kappa(d\omega_\kappa)^{N_\kappa}$$

and if the electrostatic energy terms are all at strength  $\sigma$ ,

$$B_\sigma(T) = \int \dots \int_{(v)} e^{-(W_s + \sigma W_l)/kT} \Pi_\kappa(d\omega_\kappa)^{N_\kappa}. \quad (35)$$

The average potential energy is

$$\frac{1}{B_\sigma(T)} \int \dots \int_{(v)} (W_s + \sigma W_l) e^{-(W_s + \sigma W_l)/kT} \Pi_\kappa(d\omega_\kappa)^{N_\kappa},$$

and of this we take the part

$$\frac{\sigma}{B_\sigma(T)} \int \dots \int_{(v)} W_l e^{-(W_s + \sigma W_l)/kT} \Pi_\kappa(d\omega_\kappa)^{N_\kappa}$$

to be the average electrostatic energy of the assembly. Keeping the distribution laws unaltered, but increasing each electrostatic term from  $\sigma$  to  $\sigma + d\sigma$  increases the average potential energy of the assembly by

$$\frac{d\sigma}{B_\sigma(T)} \int \cdot \cdot \cdot \int W_i e^{-(W_i + \sigma W_i)/kT} \Pi_\kappa(d\omega_\kappa) N_\kappa.$$

The total work required to build up the electrostatic force system by a reversible isothermal process is therefore again

$$- kT \int_0^1 \frac{d}{d\sigma} \log B_\sigma(T) d\sigma$$

where  $B_\sigma(T)$  is now given by (35). The equality of the reversible isothermal work of building up the electrostatic energy (or charges) with the increase in  $-T\Psi$  or  $A$  follows as before.

The application of this theorem to electrolyte theory is immediate. We have seen that our definition of  $W_{\alpha\beta}$  is such that its gradient gives the average value of the force between an  $\alpha$  and  $\beta$  so that  $W_{\alpha\beta}$  itself gives the average work required to bring up a  $\beta$  from infinity in the field of the  $\alpha$ . By (30) the average potential at the centre of an  $\alpha$  ion is  $-\kappa z_\alpha \epsilon / D$ . If all the charges are reduced to the fraction  $t$ , then this potential is reduced to the fraction  $t^2$ , since  $\kappa \propto \epsilon$ . The work done on the assembly in bringing up a further charge  $z_\alpha \epsilon dt$  is therefore

$$- \frac{\kappa z_\alpha^2 \epsilon^2}{D} t^2 dt.$$

Summed over all ions this gives an isothermal reversible expenditure of work,

$$\left( - \frac{\kappa \epsilon^2}{D} \sum_\alpha N_\alpha z_\alpha^2 \right) t^2 dt.$$

If  $\Psi_e$  is the extra electrostatic term in the characteristic function, then

$$\Psi_e = \frac{\kappa \epsilon^2}{3DT} (\sum_\alpha N_\alpha z_\alpha^2), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (36)$$

which is the standard result. It will be observed that it is  $\Psi_e$  not  $U_e$ , the extra internal energy due to the electrostatic forces, which is primarily determined by the theory, and that all questions of the temperature variation of  $D$  in the formation of  $\Psi_e$  are irrelevant. When required  $U_e$  is given at once by the thermodynamic relation,

$$U_e = T^2 \frac{\partial \Psi_e}{\partial T}.$$

The temperature variability of  $D$  is here important, and the value of  $U_e$  was wrongly given in the earlier work on this theory.<sup>5</sup>

### Summary and Conclusion.

We have in this article developed the theory of Debye and Hückel from the fundamental principles of statistical mechanics, using the method of Gibbs. The equations of Poisson and Boltzmann can be legitimately used together, provided a certain fluctuation term can be ignored as small. This is legitimate for dilute solutions, but it remains doubtful whether the more elaborate formulæ can be quantitatively correct.

<sup>5</sup> For a correct account see Bjerrum, *Z. physik. Chem.*, 119, 145 (1926).

The introduction of the dielectric constant makes use of a process of averaging in steps, which is illegitimate, though probably not seriously in error, and should be replaced if possible by a deeper investigation, including a study of saturation effects in the polarization of the medium.

It is shown directly from statistical theory that the thermodynamic function determinable from the analysis of Debye and Hückel is the characteristic function for which the temperature variation of  $D$  is irrelevant. The value given for this function by Debye and Hückel is correct, and other thermodynamic properties of the solution must be deduced from it by the standard processes of thermodynamics.

*Note added 3rd May, 1927.* An investigation with the same objects has recently been given by Kramers.<sup>6</sup> This author also relates the theory of Debye and Hückel to the phase integral of Gibbs, but by an entirely different method which seems more powerful. The reader is referred to the paper for details.

<sup>6</sup> *Amsterdam Proc.*, 30, 145 (1927).

## NOTE ON THE INTERIONIC ATTRACTION THEORY OF DEBYE AND HÜCKEL.

BY D. L. CHAPMAN.

*Received 30th March, 1927.*

Attempts have from time to time been made to explain the divergence of the properties of strong electrolytes from the laws which approximately hold in the case of slightly ionised substances. The latest theory is that of Debye and Hückel.<sup>1</sup> The theory is simple and the assumed postulates few in number.

To quote the words of A. A. Noyes who has given an account of the theory.<sup>2</sup> "The fundamental idea underlying the treatment of Debye and Hückel is that owing to the electrical attraction between the positive and negative ions, there are on an average in the neighbourhood of any ion more ions of unlike sign than of like sign; and that consequently when a solution is diluted, the separation of the ions involves doing internal work against this electrical attraction and a corresponding increase in the energy content of the solution."

I have found a difficulty in understanding that part of the theory which relates to ions of small dimension. To explain this difficulty it will be sufficient only to consider the case of a uni-univalent electrolyte.

Debye and Hückel determine the mean distribution of the ions surrounding a selected ion by the application of the so-called Boltzmann principle and Poisson's equation. If  $\psi$  is the mean potential at a point distant,  $r$ , from a central positive ion, then by the Boltzmann principle the number of positive and negative ions respectively present in an element

of volume,  $d\tau$ , at the point will be  $ne^{-\frac{e\psi}{kT}}d\tau$  and  $ne^{\frac{e\psi}{kT}}d\tau$ , where  $n$  is the number of ions in unit volume of the solution,  $e$  the magnitude of the charge in electrostatic units of an ion,  $k$  Boltzmann's constant, and  $T$  the absolute temperature. The density  $\rho$  of the charge at the point is obviously

<sup>1</sup> *Physik. Z.*, 1923, 24, 185.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1924, 46, 1080.

$n\epsilon\left(e^{-\frac{e\psi}{kt}} - e^{\frac{e\psi}{kt}}\right)$ . Substituting this value of  $\rho$  in Poisson's equation, we obtain

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} = \frac{4\pi n\epsilon}{D} \left( e^{\frac{e\psi}{kt}} - e^{-\frac{e\psi}{kt}} \right) \quad (1)$$

where  $D$  is the dielectric constant of the solvent.

If we neglect all terms of higher order than the first in the expansion of the exponential terms of the above equation, we obtain

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} = \frac{8\pi n\epsilon^2 \psi}{Dkt} \quad (2)$$

The authors state in a footnote: "We have investigated the influence of the higher terms in the expansion of  $e^{\frac{e\psi}{kt}} - e^{-\frac{e\psi}{kt}}$  and have thereby been able to show that this influence on the final result is very small. For the sake of brevity these calculations are omitted from this communication."

It is however difficult to see how the approximation can be justified in the case of very small ions.

To (2) there is a simple general solution, namely,

$$\psi = C \frac{e^{-\kappa r}}{r} + C' \frac{e^{\kappa r}}{r} \quad (3)$$

where

$$\kappa^2 = \frac{8\pi n\epsilon^2}{Dkt}$$

$C'$  is zero since otherwise the potential would be infinity at an infinite distance, and the constant  $C$  has the value  $\frac{\epsilon}{D}$ , because (as the authors state) the potential must reduce to that caused by the central ion when the concentration is infinitesimal and  $k = 0$ .

Therefore for the particular case under consideration the solution becomes

$$\psi = \frac{\epsilon}{Dr} e^{-\kappa r} \quad (4)$$

From this result the potential due to the atmosphere of ions surrounding the selected ion is found by subtracting from the potential due to the whole system that due to the central ion. We thus obtain

$$\frac{\epsilon}{Dr} (e^{-\kappa r} - 1)$$

which becomes when  $r$  is small

$$-\frac{\epsilon\kappa}{D},$$

and this is the potential due to the atmosphere of ions at the point occupied by the central ion. Then from the theory of potential the work required to remove all the ions in the solution to infinity is  $\frac{1}{2} \sum \frac{e^2 \kappa}{Dr}$ . Under the heading

"Ionendurchmesser verschwindend" the authors gave the above result as the solution of the problem. Nevertheless if the ions are point charges they cannot (under the joint operation of the Boltzmann principle and of electrostatic forces only) be distributed in the manner portrayed. For consider two ions of opposite sign. The probability that the negative ion will

be found at a distance between  $r$  and  $r + dr$  from the positive ion is  $4\pi r^2 C e^{\frac{e^2}{Dk^2}} dr$ , and therefore the probability that it will be found in a sphere of radius  $r$  having its centre at the positive ion is  $4\pi C \int_0^r r^2 e^{\frac{e^2}{Dk^2}} dr$ . The probability that it will be found in the shell of radii  $r$  and  $R$  is

$$4\pi C \int_r^R r^2 e^{\frac{e^2}{Dk^2}} dr.$$

But

$$\frac{\int_0^r r^2 e^{\frac{e^2}{Dk^2}} dr}{\int_r^R r^2 e^{\frac{e^2}{Dk^2}} dr} = \infty \quad . \quad . \quad . \quad (5)$$

From which it follows that the ions cannot separate after having once united. Furthermore if the ions are not actually dimensionless but very small, the ratio of the probability that the negative ion would be found in the small sphere of radius  $r$  to the probability that it would be found in the shell of radii  $r$  and  $R$  would be given by the quotient obtained by changing the limits of the numerator of (5) from 0 and  $r$  to  $\epsilon$  and  $r$  where  $\epsilon$  is a very small distance, and this quotient would be a large quantity provided that  $R$  was of moderate dimensions. Therefore the time during which the ions are united would be very large in comparison with the time during which they are dissociated. Such a distribution could not result in potentials given by equation (4) or to the densities of the two classes of ions calculated from these potentials. The inconsistency of the conclusion expressed by equation (5) with the result of Debye and Hückel can be accounted for by the fact that they made the assumption that

$$e^{\frac{e\psi}{kT}} - e^{\frac{e\psi}{kT}} \approx \frac{2e\psi}{kT}.$$

## SOME ANOMALIES IN THE THEORY OF SOLUTION OF STRONG ELECTROLYTES AND THEIR EXPLANATION.

BY NIELS BJERRUM.

1. Thanks to Debye and Huckel's well-known papers of 1923<sup>1</sup> the theory of the complete dissociation of strong electrolytes has at last been generally accepted. The formulæ developed by Debye and Huckel account satisfactorily for most of the so-called anomalies in dilute solutions of strong electrolytes. A few less known anomalies, however, remain as yet unexplained. These I intend to discuss and to endeavour to clear up.

2. Firstly, we have no satisfactory theory for the heat of dilution of strong electrolytes. From Richards and Rowe's<sup>2</sup> measurements it is possible to compute for 13 uni-univalent electrolytes the value of  $U_c - U_{0.139}$ ,  $U_c$  being the heat of dilution developed by adding a large amount of water

<sup>1</sup> *Physik. Z.*, **24**, 185, 305 (1923).

<sup>2</sup> *J. Amer. Chem. Soc.*, **42**, 1121 (1920); **43**, 770 (1921).

to a  $c$  molar solution containing 1 grammole electrolyte and  $U_{0.139}$  being the corresponding heat for a 0.139 molar solution.<sup>3</sup> In Fig. 1 these values are plotted against  $\sqrt{c}$ .

As seen from Fig. 1  $U_c - U_{0.139}$  varies greatly from salt to salt. In

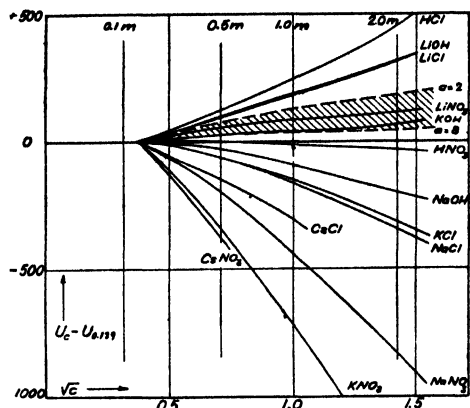


FIG. 1.—Heat of dilution of 13 uni-univalent electrolytes according to Richards and Rowe. The shaded area between the two dotted curves  $a = 2$  and  $a = 8$  represents the theoretical values according to formula (5) for uni-univalent electrolytes with ion diameters between 2 and 8 Ångström.

$D$  is the dielectric constant of the solvent,  $e$  the electronic charge,  $k$  Boltzmann's constant,  $N$  Avogadro's number,  $T$  the absolute temperature. From this formula or  $\ln f_i$  the following expression has previously<sup>3</sup> been deduced for the heat of dilution  $U_c$  of a uni-univalent electrolyte:

$$U_c = -2RTA \frac{\sqrt{2c}}{1 + Ba\sqrt{2c}} \left( 1 + \frac{T}{D} \frac{dD}{dt} \right) \quad (4)$$

or at 18° ( $a$  measured in Ångström units and  $U_c$  in calories):

$$U_c = 418 \frac{\sqrt{c}}{1 + 0.327 a \sqrt{c}} \quad (5)$$

In Fig. 1 the two dotted curves reproduce the theoretical values of  $U_c - U_{0.139}$  according to (5) for  $a = 2$  and  $a = 8$  corresponding to reasonable extreme values for the size of the ions. One would thus expect all experimental curves to run in the shaded area between these two curves. This, however, is not at all the case.

The anomalous behaviour of the heat of dilution is, perhaps, even more clearly manifested by the fact that it varies with the size ( $a$ ) of the ions in a direction opposite to that predicted by equation (5).

By comparing the freezing-point depressions of various uni-univalent electrolytes, it is possible to arrange them in the order of their  $a$ -values. In this way the following order has been determined:—<sup>4</sup>

<sup>3</sup> Bjerrum, *Z. physik. Chem.*, **119**, 158 (1926).

<sup>4</sup> Compare Bjerrum, *Z. anorg. Chem.*, **129**, 331-34 (1923).

HCl (5.2),<sup>5</sup> LiCl, HNO<sub>3</sub>, KOH, LiNO<sub>3</sub>, NaOH, NaCl (4.02),<sup>6</sup> KCl (3.40),<sup>6</sup> CsCl, NaNO<sub>3</sub>, KNO<sub>3</sub> (0.43),<sup>6</sup> CsNO<sub>3</sub>.

In a few cases the values of  $a$  in Ångström units are given in brackets.

This order corresponds to the succession of the salts arranged according to decreasing heats of dilution. Only two pairs of salts are inverted (LiNO<sub>3</sub> - HNO<sub>3</sub> and KCl - NaCl). Contrary to the prediction of formula (5), however, the electrolytes corresponding to large  $a$ -values are characterised by large heats of dilution and the electrolytes with small  $a$ -values by small (negative) heats of dilution.

Thus at the concentrations here discussed ( $c > 0.139$  m.) the anomaly is very pronounced and formula (5) is without any value.<sup>7</sup>

3. Another anomaly is shown by the partition coefficients of ions between different solvents. From the solubility of potassium chloride in water and in alcohol, it is possible to compute the partition coefficient  $V$  of this salt between water and alcohol. Correcting to infinite dilution by means of our knowledge of the activity coefficients of ions we obtain as a mean value of the partition coefficient for chloride ion and potassium ion:

$$\frac{c_{\text{water}}}{c_{\text{alcohol}}} = V = 10^{3.3} \quad . \quad . \quad . \quad (6)$$

We shall use the expression "partition exponent" for  $\log_{10} V$  and denote it by the letter  $P$ . Thus:

$$P(\text{KCl}) = \log_{10} V = 3.3 \quad . \quad . \quad . \quad (7)$$

The potassium ion and the chloride ion have an argon-like structure, but are electrically charged. Were it not for their charge, we should expect them to have the same partition coefficient as argon. According to determinations of Lannung as yet unpublished the partition exponent of argon between water and alcohol is

$$P(\text{Argon}) = -0.8 \quad . \quad . \quad . \quad (8)$$

Consequently we may estimate that the effect of the electric charges on the partition exponent of  $\text{K}^+$  and  $\text{Cl}^-$  is an increase of the following size:

$$P_e(\text{KCl}) = 3.3 - (-0.8) = 4.1 \quad . \quad . \quad . \quad (9)$$

A spherical ion with radius  $r$  and electric charge  $e$  in a medium with the dielectric constant  $D$  has an electric energy,<sup>8</sup>

$$\frac{e^2}{2rD}.$$

As the dielectric constant of alcohol ( $D_A$ ) is smaller than that of water ( $D_{\text{H}_2\text{O}}$ ) the electric work required to remove an ion from water to alcohol is positive and has the value,

$$\frac{e^2}{2r} \left( \frac{1}{D_A} - \frac{1}{D_{\text{H}_2\text{O}}} \right).$$

Corresponding to this work we may expect in the partition exponent of an ion between water and alcohol an electric term  $P_e$  given by

$$P_e = \frac{e^2}{2rkT} \left( \frac{1}{D_A} - \frac{1}{D_{\text{H}_2\text{O}}} \right) \log_{10} e \quad . \quad . \quad . \quad (10)$$

<sup>5</sup> Estimated from the data of Scatchard, *J. Amer. Chem. Soc.*, **47**, 641 (1925).

<sup>6</sup> Bjerrum, *Kgl. Danske Vid. Selsk. Mat.-fys. Medd.* **7**, No. 9, 12 (1926).

<sup>7</sup> Compare also Nernst and Orthmann, *Sitzber. Acad.*, Berlin, 1926, 51.

<sup>8</sup> Born, *Z. f. Physik.*, **1**, 45 (1920).

Introducing numerical values for  $\epsilon$ ,  $k$ ,  $T$ ,  $D_A$ ,  $D_{H_2O}$  and measuring  $r$  in Ångström units we obtain:

$$P_e = \frac{3.15}{r} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

For the ions of potassium chloride  $r$  is  $1.57\text{Å}$ . (calculated from the distance  $3.17\text{Å}$ . between the ions in a KCl-crystal). Consequently for these ions we obtain:

$$P_e(\text{KCl}) = 2.0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The experimental value of  $P_e(\text{KCl})$  being, according to equation (9),  $4.1$  we meet with an obvious anomaly. This instance typifies a general anomaly: the effect of the electric charge on the partition coefficient of ions between water and alcohol is always greater than is to be expected from formula (11).

4. As a third anomaly may be mentioned the small Soret-effect of many electrolytes.

Thus the concentration gradient produced by maintaining a temperature difference between the two ends of a solution of potassium chloride is remarkably small. At room temperature Chipman<sup>9</sup> has found for KCl:

$$\frac{1}{c} \frac{dc}{dT} = \text{about } -0.00015$$

$$\text{or} \quad \frac{d \ln c}{d \ln T} = -0.043 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

For a gas in a wide tube, if a temperature difference is maintained between the ends, the pressure is the same throughout. If analogously in the case of an ideal solution the osmotic pressure is the same throughout, we shall have  $cT = \text{constant}$ <sup>10</sup> and consequently:

$$\frac{d \ln c}{d \ln T} = -1 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If the gas is contained in a narrow tube, whose width is considerably less than the mean free path of the molecules, the pressure is inversely proportional to the square root of the temperature.<sup>11</sup>

It is perhaps more reasonable to apply this result than the former one to the molecules of a solute, moving in the small interstices between the molecules of the solvent. Then for a solute we may expect  $c^2T = \text{a constant}$  or

$$\frac{d \ln c}{d \ln T} = -\frac{1}{2} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The electric work needed to transfer an ion with radius  $r$  from a medium with a dielectric constant  $D$  to another with a dielectric constant  $D + dD$  is:

$$- \frac{\epsilon^2}{2rD} \frac{dD}{D},$$

corresponding to an electric term in the partition exponent (the concentration in the  $D + dD$ -medium in the numerator of the partition coefficient):

$$P_e = \frac{\epsilon^2}{2rDkT} \frac{dD}{D} \log_{10} e \quad . \quad . \quad . \quad . \quad (16)$$

<sup>9</sup> Chipman, *J. Amer. Chem. Soc.*, **48**, 2577 (1926).

<sup>10</sup> Van't Hoff, *Z. physik. Chem.*, **1**, 487 (1887).

<sup>11</sup> Knudsen, *Ann. d. Physik.* (4) **31**, 25, 633 (1910).

Consequently we may expect in the expression  $\frac{d\ln c}{d\ln T}$  for the Soret-effect an electric term of the size :

$$\frac{\epsilon^2}{2rDkT} \frac{d\ln D}{d\ln T}$$

and the whole Soret-effect becomes :

$$\frac{d\ln c}{d\ln T} = -0.5 + \frac{\epsilon^2}{2rDkT} \frac{d\ln D}{d\ln T} \quad (17)$$

For water at  $18^\circ$   $d\ln D/d\ln T$  is  $-1.315$  and  $\epsilon^2/2rDkT = 3.53/r$ . Thus the whole Soret-effect ought to be :

$$\frac{d\ln c}{d\ln T} = -0.5 - \frac{4.6}{r} \quad (18)$$

For potassium chloride ( $r = 1.57$ ) we obtain :

$$\frac{d\ln c}{d\ln T} = -3.4 \quad (19)$$

a result absolutely incompatible with the observed value  $-0.043$ .

5. Let us see how these anomalies may be explained. We will firstly consider the partition coefficient anomaly.

From the great effect of the electric charge on the partition coefficient between water and alcohol, it seems reasonable to conclude that the electric energy of an ion in a dielectric is greater than indicated by Born's formula.

Assuming the anomaly coefficient  $F$  (the ratio between the actual value of the energy and the value calculated according to the expression  $\epsilon^2/2rD$ ) to be the same in water and alcohol, it must for the ions of potassium chloride be on the average about 2 in these solvents. From this we may conclude that it is not permissible to use the normal macroscopic dielectric constant of the solvent in the immediate neighbourhood of an ion. If inside a sphere of radius  $2r$  round the ion we assume a dielectric constant three times smaller than the normal one we obtain an electric energy  $2 \cdot \epsilon^2/2rD$ , and this will account for the too great effect of an electric charge on the partition coefficient.

The object of this calculation is merely to give an idea of the change of the dielectric constant in the neighbourhood of an ion, which needs to be assumed in order to explain the anomaly. Of course in reality we have to expect the decrease of the dielectric constant to be continuous and steadily increasing as we approach to the ion.

It is possible to describe the anomaly under discussion by saying that the effective radii of  $K^+$  and  $Cl^-$  in water and in alcohol are but the half of their true radii, computed from crystal structure.

Recently T. J. Webb<sup>12</sup> has calculated the free energy of an ion in water, taking into consideration the dipole structure of the water molecules. For ions of the size  $r = 1.55 \text{ \AA}$ , corresponding approximately to  $K^+$  and  $Cl^-$ , he obtained an energy corresponding to anomaly factor  $F = 7$ . Considering the uncertain nature of Webb's assumptions concerning the dipole structure of water this result seems not incompatible with our ideas.

6. A variation of the anomaly coefficient  $F$  with radius of the ion and with temperature is to be expected. For large ions and at high temperatures the coefficient will presumably approach to 1. Through a study of ionic partition coefficients of different ions and at different temperatures it

<sup>12</sup> Webb, *J. Amer. Chem. Soc.*, **48**, 2589 (1926).

is possible to corroborate this assumption. Such a research is being carried out, but it is not as yet possible to give any results.

The smallness of the Soret-effect of electrolytes seems, however, to support the idea of the anomaly coefficient  $F$  decreasing with increasing temperature.

Introducing in our previous formula for the Soret-effect the anomaly coefficient  $F$  we obtain :

$$\begin{aligned}\frac{d\ln c}{d\ln T} &= -0.5 - \frac{1}{kT} \frac{d}{d\ln T} \left( \frac{\epsilon^2}{2rD} F \right) \\ &= -0.5 + \frac{\epsilon^2}{2kTrD} F \frac{d\ln D}{d\ln T} - \frac{\epsilon^2}{2kTrD} F \frac{d\ln F}{d\ln T} . \quad . \quad . \quad (20)\end{aligned}$$

For potassium chloride in water at  $18^\circ \text{C}$ . we obtain

$$\frac{d\ln c}{d\ln T} = -0.5 - 4.6 \times 1.315 - 4.6 \frac{d\ln F}{d\ln T} . \quad . \quad (21)$$

According to Chipman the Soret-effect for potassium chloride is

$$\frac{d\ln c}{d\ln T} = -0.043 . \quad . \quad . \quad (22)$$

From the equations (21) and (22) we calculate

$$\frac{d\ln F}{d\ln T} = -1.414 . \quad . \quad . \quad (23)$$

This temperature coefficient for the anomaly coefficient seems *a priori* not unreasonable. It then follows that  $F$  decreases from 2 at  $18^\circ \text{C}$ . to 1.41 at  $100^\circ \text{C}$ .

7. Without going into details I wish to mention two other anomalies which become comprehensible on taking into consideration the decrease of the dielectric constant in the immediate neighbourhood of an ion.

According to Drude and Nernst<sup>13</sup> the contraction on solution of a salt in water may be explained as a consequence of the attraction of the dielectric water by the ions, producing a strong compression in the immediate neighbourhood of the ions. Højendahl<sup>14</sup> has tried to estimate this contraction, but has obtained too small values (for a gram mol KCl about 0.5 c.c. instead of 12 c.c.). If, however, as Højendahl remarked in a discussion, the dielectric constant decreases in the immediate neighbourhood of an ion the contraction will be much greater. The contraction will be augmented not only because the contraction is inversely proportional to the dielectric constant of the medium, but also because a decrease of the dielectric constant in the neighbourhood of the ion has a strongly increasing effect on the attraction of the dielectric by the ion.

In a similar way the existence of a negative heat capacity of ions in aqueous solution<sup>15</sup> may be made comprehensible by considering the electric energy of the ion in aqueous solutions and its great negative temperature coefficient.

8. Finally let us see how we may make use of our ideas concerning the dielectric constant in the immediate neighbourhood of an ion to explain the heats of dilution of electrolytes.

The deduction of the expression (4) for the heat of dilution is based on

<sup>13</sup> Z. physik. Chem. **15**, 79 (1894).

<sup>14</sup> Private communication.

<sup>15</sup> Lewis and Randall, "Thermodynamics," pp. 84-85, 1923, New York, by McGraw-Hill Book Company.

the tacit assumption that the ion diameter  $a$  in Debye and Hückel's formula (1) for the activity coefficient  $f$  is independent of the temperature.

The  $a$ -values to be used in formula (1) in order to get a close agreement with the experimental activity coefficient values, however, scarcely represent the true ion dimensions. For electrolytes such as LiCl, NaCl,  $a$  is greater than the distance between the ions in the crystals of the same salts and in a similar way for HCl  $a$  is much greater than is to be expected. These great  $a$ -values have been explained by hydration; accepting this explanation we have to expect a decrease of these  $a$ -values, as of the hydration itself, with increasing temperature. On the other hand, the  $a$ -values of nitrates are too small to represent the true ion dimensions or even only true minimum distances between unsymmetrically placed charges of the ions. If the electric force between ions close to each other is greater than indicated by the expression

$$\frac{e^2}{r^2 D},$$

( $D$  the normal macroscopic dielectric constant of the solvent), it means in the main that the  $a$ -value to be used in formula (1) is but an effective value smaller than the true one. This consideration makes the smallness of the experimental  $a$ -values of nitrates and similar salts comprehensible and leads to the assumption that these small  $a$ -values may increase with increasing temperature.

If  $a$ , however, is dependent on the temperature the earlier expression for the heat of dilution  $U_c$  must be supplemented by a second term  $\Delta U_c$ :

$$\Delta U_c = -4RTA \frac{da}{d \ln T} \frac{1}{c} \int_0^c \frac{Bc}{(1 + Ba\sqrt{2c})^2} dc \quad . \quad . \quad (24)$$

$U'_c$  being the heat of transference of one gram mole ion from a great quantity of a solution of concentration  $c$  to infinite dilution, we have

$$U'_c = -RT^2 \frac{d \ln f}{dT} \quad . \quad . \quad . \quad (25)$$

and from  $U'_c$  we obtain  $U_c$  (for a binary electrolyte) by means of the formula

$$U_c = \frac{2}{c} \int_0^c U'_c dc \quad . \quad . \quad . \quad (26)$$

By means of equations (25) and (26) equation (24) is easily deduced.

If  $Ba\sqrt{2c} \ll 1$  one may neglect the second term of the denominator of the integrand in (24); doing this, introducing numerical values for  $R$ ,  $T$ ,  $A$  and  $B$ , and measuring  $a$  in Angström we obtain

$$\Delta U_c = -217 \frac{da}{d \ln T} c \quad . \quad . \quad . \quad (27)$$

Thus the term  $\Delta U_c$  to add to expression (5) for the heat of dilution is proportional to the concentration  $c$  and its sign is positive when  $a$  decreases and negative when  $a$  increases with increasing temperature. Therefore this term  $\Delta U_c$  will explain at last qualitatively the difference  $\Delta(U_c - U_{c,139})$  between the values of  $U_c - U_{c,139}$  experimentally determined by Richards and Rowe and those theoretically estimated from formula (5). As pointed out before this difference  $\Delta(U_c - U_{c,139})$  is positive for ions with large  $a$ -values for which we have to expect a decrease of  $a$  with increasing temperature and negative for ions with small  $a$ -values for which we have to expect decreasing  $a$ -values with increasing temperature.

In Fig. 2 the difference  $\Delta(U_0 - U_{0.139})$  is plotted against  $c$  (in the calculation of the theoretical values of  $U_0 - U_{0.139}$  an average value of  $a = 3.5$  Å was used). From Fig. 2 may be seen that  $\Delta(U_0 - U_{0.139})$

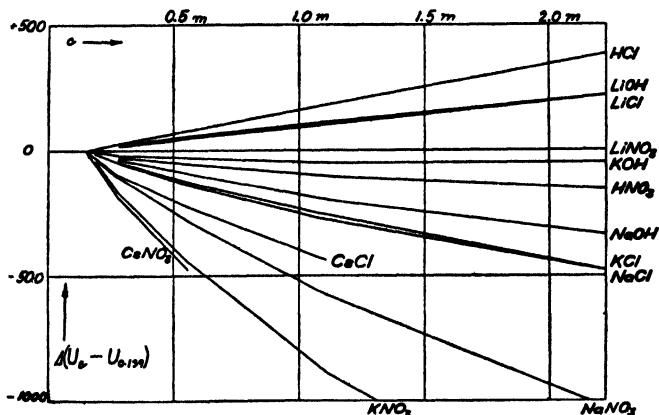


FIG. 2.—The part of the experimental heat of dilution  $U_0 - U_{0.139}$  not explained by formula (4) plotted against concentration.

increases roughly proportionally to  $c - 0.139$  as it should according to equation (27). The proportionality factor  $k$ , defined by

$$k = \frac{\Delta(U_{0.555} - U_{0.139})}{0.555 - 0.139} \quad (28)$$

should according to equation (27) be

$$k = -217 \frac{da}{d \ln T} \quad (29)$$

In Table II, column 2, are given the experimentally determined  $k$ -values, and in column 3 the values of  $\frac{da}{d \ln T}$  calculated from these values by means of equation (29).

TABLE II.

	$k$ .	$\frac{da}{d \ln T}$ .
HCl . . . .	+ 187	- 0.86
LiOH . . . .	+ 135	- 0.62
LiCl . . . .	+ 120	- 0.55
LiNO <sub>3</sub> . . . .	0	0
KOH . . . .	- 27	+ 0.12
HNO <sub>3</sub> . . . .	- 54	+ 0.25
NaOH . . . .	- 93	+ 0.43
KCl . . . .	- 130	+ 0.60
NaCl . . . .	- 138	+ 0.64
CsCl . . . .	- 228	+ 1.05
NaNO <sub>3</sub> . . . .	- 281	+ 1.29
KNO <sub>3</sub> . . . .	- 448	+ 2.06
CsNO <sub>3</sub> . . . .	- 477	+ 2.20

These values of  $da/d \ln T$  are satisfactory in so far as for hydrated electrolytes with large  $a$ -values (HCl, LiOH, LiCl),  $a$  decreases with increasing

temperature, whereas for non-hydrated electrolytes with small  $\alpha$ -values  $\alpha$  increases with increasing temperature.

9. It is, however, not possible to develop a quantitative theory on the basis of equation (29). Firstly we have neglected the second term of the denominator in equation (24) which at the concentrations considered is unjustifiable. Secondly the equation (1) of Debye and Hückel for the activity coefficient is scarcely exact at higher concentrations. Thus according to Hückel<sup>16</sup> it is necessary to take into consideration the effect of the electrolytes on the dielectric constant of the solution. Doing this Hückel introduces in the formula for  $\ln f$  a second term approximately equal to

$$\frac{\epsilon^2}{2kTr} \left( \frac{1}{D_0} - \frac{1}{D_e} \right) \quad . \quad . \quad . \quad . \quad (30)$$

( $D_0$  and  $D_e$  are the dielectric constants of water and solution). The origin of this term may be easily understood after our discussion of the theory for ionic partition exponents.

Supposing  $(D_0 - D_e)/D_e$  to be proportional to the concentration, we may write

$$\frac{D_0 - D_e}{D_e} = \alpha c \quad . \quad . \quad . \quad . \quad (31)$$

and assuming the radius  $r$  of the ion and the relative depressing effect  $\alpha$  of the electrolyte on the dielectric constant to be independent of temperature, by means of equations (25) and (26) we obtain in the expression for  $U_e$  the heat of dilution of a univalent electrolyte in water at 18° C. a third term:

$$\Delta'U_e = RT \frac{\epsilon^2}{2kTD_0} \frac{d \ln D_0}{d \ln T} T \frac{\alpha}{r} c \quad . \quad . \quad . \quad . \quad (32)$$

Introducing numerical values we get

$$\Delta'U_e = - 572 \frac{\alpha}{r} c \quad . \quad . \quad . \quad . \quad (33)$$

This formula, however, does not explain the differences between the values of the heat of dilution of different electrolytes. In order to explain the change of  $\ln f$  with concentration it is necessary to assume positive  $\alpha$ -values for hydrogen chloride and for lithium salts and negative  $\alpha$ -values for nitrates. Thus in all these cases expression (33) gives to  $\Delta'U_e$  a sign inconsistent with the experimental data of Richards and Rowe.

If, however,  $r$  is considered as dependent on the temperature, we obtain another expression for  $\Delta'U_e$ .

As in the theory for the partition coefficients we introduce for the electric energy of an ion with the true and constant radius  $r$  the expression

$$-\frac{\epsilon^2}{2rD} F \quad . \quad . \quad . \quad . \quad (34)$$

where  $F$  is the anomaly coefficient dependent on temperature.

Then we obtain

$$\Delta'U_e = RT \frac{\epsilon^2}{2rkTD_0} F \alpha \left( \frac{d \ln TD_0}{d \ln T} - \frac{d \ln F}{d \ln T} \right) c \quad . \quad . \quad . \quad (35)$$

Introducing numerical values we obtain for a univalent electrolyte in aqueous solution at 18° C.

$$\Delta'U_e = 1810 \frac{\alpha F}{r} \left( -0.315 - \frac{d \ln F}{d \ln T} \right) c \quad . \quad . \quad . \quad (36)$$

According to this expression we may explain the sign of the experimentally determined values of the heat of dilution for hydrogen chloride, lithium salt and nitrates as a consequence of  $d\ln F/d\ln T$  being smaller than  $-0.315$ .

A quantitative theory is however not as yet possible.

Using for potassium chloride  $a = 0.25^{17}$  and, in agreement with our former developments,

$$\frac{3.15}{r} F = 4.1 \quad . \quad . \quad . \quad . \quad . \quad (37)$$

we obtain

$$\Delta U_c(\text{KCl}) = 589 \left( -0.315 - \frac{d\ln F}{d\ln T} \right) c \quad . \quad . \quad . \quad (38)$$

Richards and Rowe's experimental determinations lead to

$$\Delta U_c(\text{KCl}) = -130 c \quad . \quad . \quad . \quad . \quad . \quad (39)$$

From equation (38) and (39) we deduce

$$\frac{d\ln F}{d\ln T} = -0.315 + \frac{130}{589} = -0.094 \quad . \quad . \quad . \quad (40)$$

This temperature coefficient is not in agreement with the temperature coefficient  $-1.421$  deduced from the Soret-effect (equation (23)).

In a quantitative theory for the heat of dilution of electrolytes it will be necessary to take into consideration not only the dependence on temperature of Hückel's extra term, but also the dependence on temperature of  $a$  in the original Debye-Hückel expression. Moreover, it will certainly be necessary to consider the direct effect of a real chemical hydration.

10. I hope later through new experimental and theoretical researches to be able to build a quantitative theory on the ideas here developed; but even in their present imperfect form these considerations seem to me of value, as showing that on the basis of the hypothesis of complete dissociation of strong electrolytes the various apparent anomalies here discussed are really to be expected. They all seem to be explicable by the obvious assumption that the effective dielectric constant decreases in the immediate neighbourhood of ions.

<sup>17</sup> See Hellmann and Zahn, *Ann. Physik*, **81**, 748 (1926).

## MIXED SOLUTIONS OF ELECTROLYTES AND NON-ELECTROLYTES.

By GEORGE SCATCHARD.

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Although we cannot devise a theoretical model which corresponds exactly to any actual liquid mixture two methods of treatment are possible. The first is to make a model which fits the known properties of the molecules as closely as possible, but which generally involves approximate mathematical methods. The second is to devise a simple model which fits the facts approximately and to determine exactly the properties of the model. The Debye theory of electrolytes as originally published<sup>1</sup> conforms

<sup>1</sup> Debye and Hückel, *Physikal. Z.*, **24**, 185 (1923).

closely to the second method, but the extensions of Debye and McAulay<sup>2</sup> and of Hückel<sup>3</sup> to variations in the dielectric constant involve both physical and mathematical approximations. It seems desirable to treat this case more rigorously, and at the same time a little more generally.

An ion is represented by an electrical charge distributed with spherical symmetry within a sphere of radius  $b$  whose dielectric constant is independent of the medium. The medium without the sphere is considered continuous and of uniform dielectric constant. With respect to interionic collisions an ion is regarded as a rigid sphere. We will call  $a$  the nearest distance of approach of another ion centre. The ion is also characterised by its effects on the dielectric constant and on the volume of the system. For a molecule of zero charge the two sizes  $a$  and  $b$  are unimportant, so a neutral molecule is characterised by its effect on the dielectric constant and volume.

The solution of the problem depends on the relative magnitudes of  $a$  and  $b$ . If  $a$  is less than  $b$  the solution is very complicated.<sup>4</sup> If  $a$  is equal to or greater than  $b$  it is much simpler. Table I. gives a list of the  $a$  and  $b$  values which have been determined.

TABLE I.  
SIZE OF IONS IN ÅNGSTRÖM UNITS (CM.  $\times 10^{-8}$ ).

	$a$ .	$b$ .	$a/b$ .		$a$ .	$b$ .	$a/b$ .
HCl	4.05 <sup>6</sup>	6.4 <sup>6</sup>	0.6	KCl	2.47 <sup>6</sup>	1.35 <sup>6</sup>	1.8
H <sub>2</sub> SO <sub>4</sub>	1.72 <sup>5</sup>	5.0	0.3	KNO <sub>3</sub>	2.13	1.7 <sup>7</sup>	1.3
LiCl	3.62 <sup>3</sup>	1.35 <sup>6</sup>	2.7	KOH	3.35 <sup>5</sup>	1.0 <sup>7</sup>	3.3
Li <sub>2</sub> SO <sub>4</sub>	3.31 <sup>5</sup>	1.3	2.5	K <sub>2</sub> SO <sub>4</sub>	2.85 <sup>5</sup>	1.4 <sup>7</sup>	2.0
NaCl	2.35 <sup>3</sup>	1.31 <sup>6</sup>	1.8	CaCl <sub>2</sub>	3.83 <sup>5</sup>	2.0	1.9
NaOH	2.87 <sup>5</sup>	1.0	2.9	SrCl <sub>2</sub>	4.39 <sup>5</sup>	1.7	2.6
Na <sub>2</sub> SO <sub>4</sub>	3.10 <sup>5</sup>	1.5	2.1	BaCl <sub>2</sub>	4.35 <sup>5</sup>	2.2	2.0

Except for the acids  $a$  is always greater than  $b$ , and in most cases it is two or three times as great.

For a simple solution it is necessary to assume that  $a$  is not less than a certain value, which is about  $2 \times 10^{-8}$  cm. for a univalent ion in water, and that the  $a$ 's are the same for all the ions in the system. This latter is probably justified for solutions of only two kinds of ions even if the diameters are different. The more general case of salt mixtures requires detailed knowledge not available at present.

For the case that  $a$  is not less than  $b$  the equation, whose derivation and application to changing salt concentration in aqueous solutions will be published elsewhere, is

$$\frac{\partial F_0}{\partial n_i} = \frac{\epsilon^2}{2D} \left[ z_i^2 \left( \frac{1}{b_i} - \frac{\kappa}{1 + \kappa a} \right) - \frac{\partial \ln D}{\partial c_i} \left( 1 - c_i \frac{\partial V}{\partial n_i} \right) \sum_{j=1}^{j=s} c_j z_j^2 \left( \frac{1}{b_j} - \frac{\kappa}{1 + \kappa a} \right) \right. \\ \left. + \frac{\kappa}{(\kappa a)^3} \frac{\partial V}{\partial n_i} \sum_{i=1}^{j=s} c_j z_j^2 \left[ 1 + \kappa a - \frac{1}{1 + \kappa a} - 2 \ln(1 + \kappa a) \right] \right] \quad (1)$$

<sup>2</sup> Debye and McAulay, *Physikal. Z.*, **26**, 22 (1925).

<sup>3</sup> Hückel, *ibid.*, **26**, 93 (1925).

<sup>4</sup> Debye and Pauling, *Journ. Amer. Chem. Soc.*, **47**, 2129 (1925).

<sup>5</sup> Harned and Åkerlöf, *Physikal. Z.*, **27**, 411 (1926).

<sup>6</sup> Scatchard, *Jour. Am. Chem. Soc.*, **47**, 2098 (1925); **49**, 217 (1927).

<sup>7</sup> Scatchard, *Chem. Rev.*, **3**, 383 (1927).

$F_e$  is the electrical contribution to the free energy of the system containing  $s$  kinds of molecules;  $n_i$  is the number of molecules of the  $i$ th kind in the system,  $c_i$  their concentration, and  $z_i$  their valence.  $e$  is the charge on a hydrogen ion,  $D$  is the dielectric constant of the system,  $V$  its volume and

$$\kappa = \left( \frac{4\pi e^2}{DkT} \frac{\sum n_i z_i^2}{V} \right)^{\frac{1}{2}}.$$

$k$  is Boltzmann's constant and  $T$  the absolute temperature.

The third term in this expression is relatively very small except for the solvent. The first term vanishes for a non-electrolyte. The second term is evidently a complicated function of the electrolyte concentration. The part in parenthesis diminishes with increasing concentration since  $\kappa$  varies as the square root of the concentration. This is compensated by an increase in the factor outside the parenthesis due to a decrease in  $D$  and probably to an increase in  $\frac{\partial \ln D}{\partial c_i}$ . The combination of these effects

makes  $\frac{\partial F_e}{\partial n_i}$  nearly proportional to the ionic strength so that the equation for infinitely dilute salt solutions serves as an approximation, and sometimes a very accurate one, up to high salt concentrations.

For electrolytes it is simplest to extrapolate to zero concentration by

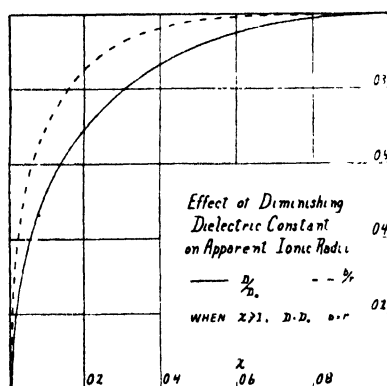


FIG. 1.

which the dielectric constant is independent of the medium. The full line in Fig. 1 illustrates such a variation in dielectric constant, and the broken line shows the ratio of the radius  $b$ , calculated from the work of charging, on the assumption of uniform dielectric constant, to the true radius  $r$ . The scale of abscissæ in ordinary length units is of course undetermined, but there are indications that the ordinary ions have radii about 0.1, so that the values of  $b$  must not be interpreted too literally as true radii. Moreover, there is no reason to suppose that these curves have the same form for all solvents; so, even if the radius  $r$  is independent of the medium, it is possible that the apparent radius  $b$  varies.

The simplified expression for  $F_e$ , the electrical contribution to the free energy of a system composed of  $n_1$  molecules of solvent,  $n_2$  of non-electrolyte solute, and  $n_3$  of an electrolyte dissociating into  $\nu$  ions of valence  $z_+$  and  $z_-$  (both taken as positive quantities), is

<sup>8</sup> Zwicky, *Physikal. Z.*, **27**, 271 (1926); Webb, *Proc. Nat. Acad. Sci.*, **12**, 524 (1926); *Journ. Amer. Chem. Soc.*, **48**, 2589 (1926).

$$F_e = \frac{\epsilon^2}{2D} \sum \frac{n_i z_i^2}{b_i} = \frac{\epsilon^2 n_0 v z_+ z_-}{2D\bar{b}} \quad (2)$$

$$\frac{\partial F_e}{\partial n_3} = \frac{\epsilon^2 v z_+ z_-}{2D\bar{b}} \quad (3)$$

$$\frac{\partial F_e}{\partial n_2} = -\frac{\epsilon^2 \mu}{D_0 \bar{b}} \frac{\partial \ln D}{\partial m} = \frac{\epsilon^2 \beta}{D_0 \bar{b}} \mu \quad (4)$$

$$\frac{\partial F_e}{\partial n_1} = \frac{\epsilon^2 w_1 \mu m}{D_0 \bar{b}} \frac{\partial \ln D}{\partial m} = -\frac{\epsilon^2 w_1 \beta}{D_0 \bar{b}} \mu m \quad (5)$$

$\mu$  is the ionic strength of the solution,  $m$  is the molality of the non-electrolyte,  $\beta = -\frac{\partial \ln D}{\partial m}$ ,  $D_0$  is  $D$  for the pure solvent, and  $w_1$  is 0.001 times the molecular weight of the solvent.

If it be assumed that there are no causes for deviation from ideality other than the electrostatic forces here considered,

$$\frac{\partial F_e}{\partial n_i} - \frac{\partial F_{e0}}{\partial n_i} = kT \ln f_i \quad (6)$$

$F_{e0}$  is the value of  $F_e$  in the standard state;  $f_i$  is the ratio of activity to mol fraction.

Most insight into the properties of non-electrolyte-electrolyte mixtures may be obtained from measurements of salt activities, but there are only a

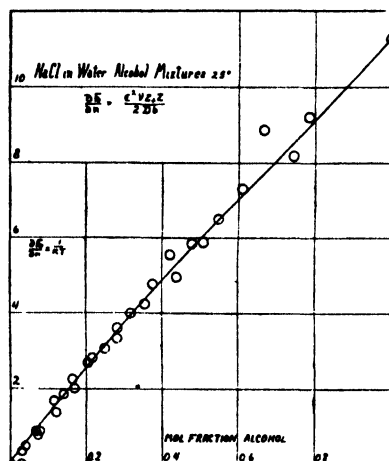


FIG. 2.

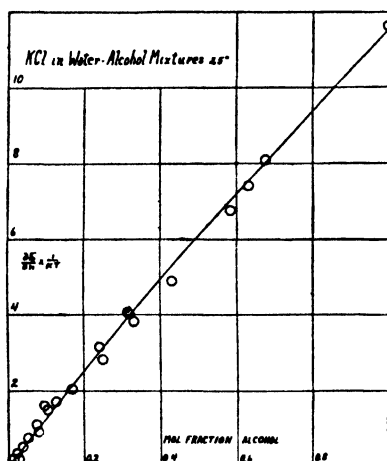


FIG. 3.

few systems upon which all the necessary measurements have been made.

$\frac{\partial F_e}{\partial n_3}$  is closely related to molal electrode potentials; it may be determined from measurements of electromotive force or of salt solubility. Fig. 2 shows the results for sodium chloride in mixtures of water and ethyl alcohol.<sup>6</sup> The curve is determined from the theory by measurements in the pure solvents and the dielectric constants of the mixtures. The agreement is extremely good. In Fig. 3 are shown similar results for potassium chloride.<sup>6</sup>

Fig. 4 represents  $\frac{\partial F_e}{\partial n}$  for hydrogen chloride in the same solvents.<sup>6</sup> The

two broken lines are the theoretical expressions for  $b = 1.65$  and  $6.40$ . Neither fits the experimental points and it is clear that the behaviour of hydrogen chloride is very different from that of sodium or potassium chlorides. The most obvious explanation is that the hydrogen ion cannot exist in solution as an isolated proton. If the hydrogen ion combines practically completely with water to form  $H_3O^+$  even in solutions containing a large excess of alcohol the full line should represent  $\frac{\partial F}{\partial n}$  for hydrogen chloride. The agreement is greatly improved. The explanation of the remaining discrepancy may lie in the neglect of an alcoholated hydrogen ion.

These figures seem to be extremely good evidence that the potassium, sodium, and chloride ions do not combine chemically with water. The difference between the two lower curves in Fig. 4 shows the effect of a single molecule of water of hydration. It is enough to ruin completely the agreement between theory and experiment for the alkali halides. The

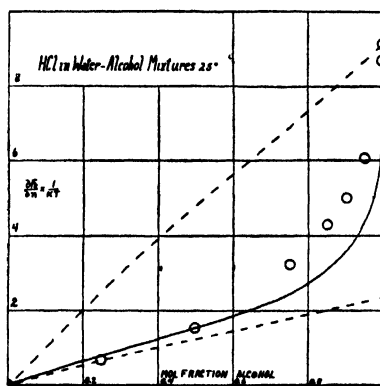


FIG. 4.

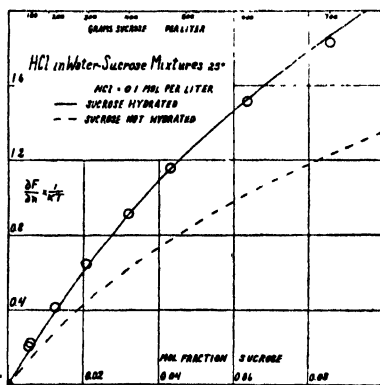


FIG. 5.

measurements do not preclude two molecules of water of hydration for the hydrogen ion, but that seems improbable from other evidence.

There is evidence also against polymerisation or compound formation between the non-electrolytes, for the curves are computed on the basis of simple molecules of  $H_2O$  and  $C_2H_5OH$ . Fig. 5 probably shows the effect of compound formation between the non-electrolytes.<sup>9</sup> It shows  $\frac{\partial F}{\partial n}$  for hydrogen chloride in tenth molal solutions of acid containing various mixtures of sucrose and water. The curves are determined from the theory and the values of the constants for water-alcohol mixtures. For the broken line it is assumed that there is no compound formation; the full line is drawn on the assumption that the sucrose is hydrated and that the mol fraction of uncombined water in solutions without acid is equal to its activity.

The expression for the solubility of a non-electrolyte in solutions of an electrolyte gives an interpretation of the constant in the law announced empirically by Setschenow<sup>10</sup> in 1892 that the solubility is an exponential function of the electrolyte concentration. The theoretical expression

<sup>9</sup> Scatchard, *J. Amer. Chem. Soc.*, **48**, 2026 (1926).

<sup>10</sup> Setschenow, *Ann. chim. et physique* (6), **25**, 226 (1892).

applies strictly only to infinitely dilute solutions, but is stretched to high salt concentrations through the compensation of several factors. Since this compensation cannot be expected to be complete in all cases it is not surprising that the deviations from Setschenow's law are sometimes considerable, particularly when the change of solubility is small. As illustrations I have chosen cases where the deviation is negligible. Fig. 6 shows results for oxygen<sup>11</sup> in solutions which show particularly well the variation in salting-out effect of different electrolytes.

Fig. 7 shows the solubility of pseudoglobulin and of egg albumin in ammonium sulphate solutions.<sup>12</sup> The slope of the curves is about ten times as great as the corresponding one for oxygen, but otherwise the solubilities of these complicated molecules follow the same law as that of the very simple ones.

$\frac{\partial F_e}{\partial n}$  for the solvent is interesting largely as a means of determining the characteristic constants of the solutes which is applicable in a very large

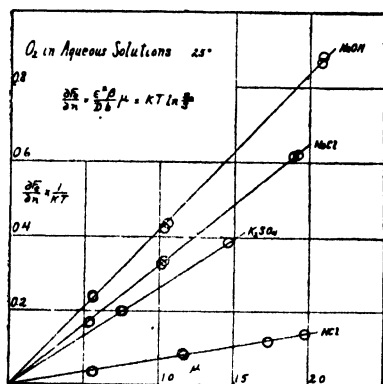


FIG. 6.

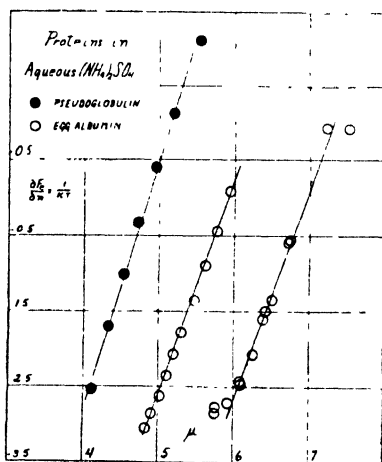


FIG. 7.

number of cases. If the solution is so dilute that the freezing-point depression may be considered proportional to  $\frac{\partial F}{\partial n_1}$  and the depression of ideal solutions may be taken as additive, it may be shown that

$$\theta_{n+s} - \theta_n - \theta_e = \frac{NT_0}{Q_0} \frac{\partial F_e}{\partial n_1} = \frac{N\epsilon^2 w_1 T_0 \beta \mu m}{Q_0 D b}$$

$\theta_{n+s}$  is the depression of the mixed solution;  $\theta_n$  that of a solution of the non-electrolyte at the same molality;  $\theta_e$  that of a solution of the electrolyte at the same ionic strength;  $N$  is Avogadro's number;  $T_0$  is the freezing-point of the pure solvent,  $Q_0$  its molal heat of fusion. Fig. 8 shows the results for solutions of ethyl alcohol with two salts.<sup>13</sup> In each case the position of the curve for the lower alcohol concentration is determined by theory from that of the higher.

<sup>11</sup> Geffcken, *Z. physikal. Chem.*, **49**, 257 (1904).

<sup>12</sup> Cohn, *Physiol. Rev.*, **5**, 410 (1925). Measurements of Chick and Martin, of Sørensen and Höyrup, and of Sørensen.

<sup>13</sup> Sachs, *Thesis*, Mass. Institute of Technology (1925).

The theory may be tested by comparison of the size of the ions computed from measurements by different methods in various systems. It

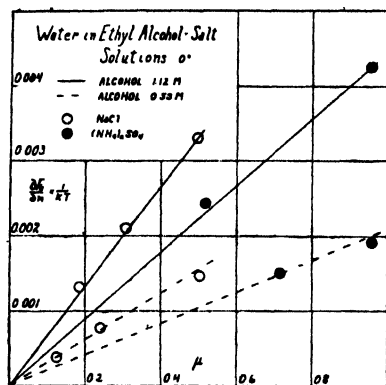


FIG. 8.

is convenient to compare  $1/b$  rather than  $b$ , for the effects, and therefore the experimental errors are proportional to it, and it is  $1/b$  which is additive for the ions. Table II. contains such a comparison. The first seven rows represent all the systems for which the dielectric constants have been directly determined. The last three are illustrative of the large group for which  $\beta$  may be computed from the salting out effect of a salt of known  $b$ , sodium chloride in this case. Hydrogen and oxygen are chosen because it seems most improbable that they show any specific interaction. The computed ionic radii are of the right order of magnitude, a few Ångström units, and the agreement between the different methods is fair. It does appear that either  $\beta$  or  $b$  is a function of the temperature, for the results obtained by combining  $\beta$  measured at room temperature and freezing-points are all higher than for those series in which all the measurements are made at room temperature.

TABLE II.  
RECIPROCAL RADII OF IONS -  $\frac{10^{-8}}{b}$ .

Method.	HCl.	LiCl.	NaCl.	KCl.
E.m.f. and salt solubility <sup>6</sup>	0.16	0.74	0.76	0.74
Freezing-point, ethyl alcohol <sup>13</sup>	—	—	1.06	1.06
"    ethyl acetate <sup>14</sup>	—	0.75	0.97	0.98
"    sucrose .	—	1.25	0.93	0.75
Solubility of ethyl acetate, 25° <sup>15</sup>	—	—	0.71	0.61
"    "    "    25° <sup>16</sup>	—	0.63	0.70	0.69
"    "    "    50° <sup>16</sup>	—	0.64	0.80	0.85
"    hydrogen, 15° <sup>17</sup>	—	0.72	(0.76)	0.80
"    oxygen, 15° <sup>11</sup>	0.17	—	(0.76)	—
"    "    25° <sup>11, 18</sup>	0.23	0.50	(0.76)	0.72

The  $\beta$  values of a few substances are given in Table III. together with 1000 times the ratio of  $\beta$  to the molecular weight. This quantity should be unity for a substance of unit density and zero dielectric constant if the dielectric constants of its mixtures with water are additive; a larger dielectric constant or density would decrease it. The value for hydrogen, and possibly for oxygen, is high because of the small density. It is interesting that the values for the proteins are very small. Their large  $\beta$

<sup>14</sup> Measurements of Rivett, *Medd. K. Vetenskapsakad. Nobelinst.*, 2, No. 9 (1913)

<sup>15</sup> Measurements of Lunden, *ibid.*, No. 15 (1913).

<sup>16</sup> Measurements of Glasstone and Pound, *J. Chem. Soc.*, 127, 2660 (1925).

<sup>17</sup> Measurements of Steiner, *Wied. Ann.*, 52, 275 (1894).

<sup>18</sup> Measurements of McArthur, *J. physical Chem.*, 20, 495 (1916).

TABLE III.

## DIELECTRIC CONSTANTS OF AQUEOUS SOLUTIONS

Solute.	Method.	$\beta$	$1000\beta/M.W.$
Hydrogen . . . . .	Solubility	0.05	25
Oxygen . . . . .	"	0.06	1.9
Ethyl Alcohol . . . . .	Direct <sup>19</sup>	0.045	1.0
Ethyl Acetate . . . . .	" <sup>20</sup>	0.09	1.0
Sucrose . . . . .	Direct <sup>20, 21</sup>	0.08	0.23
Egg albumin . . . . .	Solubility	0.6	0.02
Pseudoglobulin . . . . .	"	0.7	0.01
Urea . . . . .	Direct	- 0.04	- 0.75

values and extreme susceptibility to salting out are then dependent only or their very high molecular weights.

It has been customary to compare the effect of different salts at the same equivalent concentration rather than at the same ionic strength. So our comparisons will be in terms of  $1/b$  multiplied by half the sum of the valences of the ions. Table IV. shows this quantity for several potassium

TABLE IV.

## SALT EFFECTS OF POTASSIUM SALTS AT EQUIVALENT CONCENTRATIONS.

Salt.	$\frac{(z_+ + z_-)}{2}$	$\frac{(z_+ + z_-) \times 10^{-8}}{2b}$		
		Freezing-Point.		Gas Solubility H <sub>2</sub> or O <sub>2</sub> <sup>11, 17, 18.</sup>
		EtOH <sup>13.</sup>	EtAc <sup>14.</sup>	
K <sub>2</sub> HPO <sub>4</sub> . . . . .	1.5	1.32	—	—
K <sub>2</sub> SO <sub>4</sub> . . . . .	1.5	1.17	1.00	1.21
K <sub>2</sub> Cit . . . . .	2	1.14	—	—
K <sub>2</sub> CO <sub>3</sub> . . . . .	1.5	—	—	1.10
KOH . . . . .	1	—	—	0.96
KHCO <sub>3</sub> . . . . .	1	1.07	—	—
KCl . . . . .	1	1.06	0.98	0.76
KBr . . . . .	1	1.02	0.71	0.65
KNO <sub>3</sub> . . . . .	1	0.82	0.58	0.51
KI . . . . .	1	0.89	0.48	0.43

salts. The three series place the salts in the same order except for the nitrate and iodide, whose difference is within the experimental error. The differences from salt to salt in the three series may be due to specific effects or to experimental error. These measurements give a Hofmeister series for the anions in equilibria where colloidal and surface effects are absent, where the concentration of hydrogen ion is unimportant, and where the probability of a specific chemical action is a minimum.

The general occurrence of similar series wherever the behaviour of ions at interfaces is concerned makes it probable that the ionic radius,  $b$ , has an important influence on these effects also. Just as the precipitating action

<sup>19</sup> Nernst, *Z. physikal. Chem.*, **14**, 622 (1894).

<sup>20</sup> Debye and Sack, *Private Communication*.

<sup>21</sup> Harrington, *Physical Rev.*, **8**, 581 (1916).

of an ion on a typical sol increases more rapidly with the ionic charge than does its effect on equilibria involving molecular ions, so the surface effects appear to vary more with the ionic size than do the equilibria considered here. A more quantitative study of this relation may well increase our knowledge both of surface phenomena and of ions.

The properties of mixed solutions of electrolytes and non-electrolytes correspond to those of the model of a spherical ion in a continuous medium more closely than we should expect from the simplicity of the model. Not only is it accurate enough to serve as a means of correlating the various equilibria in such ternary systems, but it also seems probable that the deviations will lead to a new insight into the properties of the ions and that the use of the model may be extended to a study of more diverse problems.

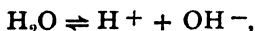
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## ON THE THERMODYNAMIC PROPERTIES OF A FEW CONCENTRATED SALT SOLUTIONS.

BY HERBERT S. HARNED.

*Received February 28th, 1927.*

By the methods of thermodynamics, the activity and stoichiometrical activity coefficient of an electrolyte in aqueous solution may be measured. This measurement gives also the activity of the water molecule. But in an aqueous salt solution, hydrogen and hydroxyl ions are present, and, if the dissociation of water be represented by the purely tentative scheme,



then according to thermodynamics, the equilibrium constant,  $K$ , of this reaction will be given by

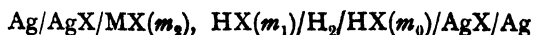
$$K = \frac{a_{\text{H}} a_{\text{OH}}}{a_{\text{H}_2\text{O}}} = \frac{\gamma_{\text{H}} \gamma_{\text{OH}} m_{\text{H}} m_{\text{OH}}}{a_{\text{H}_2\text{O}}} \quad . \quad . \quad (1)$$

where the " $a$ 's," the " $\gamma$ 's" and the " $m$ 's" are the activities, the activity coefficients and the molalities of the species denoted by subscripts. For the verification of the future theory of these solutions, it is necessary to determine accurately the activity coefficients of the ions of the dissolved salt and of the hydrogen and hydroxyl ions in a salt solution.

A brief resumé of experiments leading to a determination of these quantities will be given, and some of the more important results obtained during the course of this investigation will be considered.

### (1) The Activity Coefficients of Strong Acids in Homoanionic Salt Solutions.

The electromotive forces of the cells:



are given by the equation,

$$E_1 = 0.05915 \log \frac{\gamma_{H(S)} \gamma_{X(S)} m_1 (m_1 + m_2)}{\gamma_{H(m_0)} \gamma_{X(m_0)} m_0^2} \quad (2)$$

$$= 0.1183 \log \frac{\gamma_{HX(S)} \sqrt{m_1 (m_1 + m_2)}}{\gamma_{HX(m_0)} m_0} \quad (3)$$

where the subscript (S) refers to the acid-salt solution, the subscript ( $m_0$ ) to the pure aqueous solution of the acid, and  $\gamma_{HX}$  equals  $\sqrt{\gamma_H \gamma_X}$ .

Numerous measurements of cells of this type and similar cells containing sulphuric acid and sulphates with mercurous sulphate electrodes have been discussed elsewhere,<sup>1</sup> and, consequently, only some of the more important features regarding the activity coefficients of these acids in the homoanionic salt solutions need be summarised.

(1) The activity coefficient of a halogen acid in a solution of a halide behaves similarly to a single strong electrolyte in the pure solvent. Its activity coefficient at constant acid concentration and constant temperature first decreases, then passes through a minimum and, finally, increases upon salt addition.

(2) At a given acid and total concentration, the activity coefficients of these strong acids are greater in the solution of the salt of a given valence type which in the pure solvent has the higher activity coefficient.

(3) This fact is in accord with Hückel's theory<sup>2</sup> of the concentrated solutions whereby all activity coefficients of electrolytes at a given concentration are greater in the solution which possesses the higher electrical field strength.

(4) It has been found possible by the use of Hückel's equations to calculate the activity coefficient of hydrochloric acid in halide solutions from the data on these electrolytes in pure aqueous solutions, and *vice versa*. However, Hückel's equation for the variation of the dielectric constant of the medium cannot be the only factor to be added to the original Debye and Hückel theory since it leads to negative values for the dielectric constant in concentrated solutions of electrolytes such as lithium chloride and hydrochloric acid.

(5) The equation which results from Hückel's theory,

$$\log \gamma = \frac{-u\sqrt{2\mu_T}}{1 + A\sqrt{2\mu_T}} + B(2\mu_1) + B'(2\mu_T - 2\mu_1) - \log \left( 1 + \frac{M_0}{1000} \nu m_T \right) \quad (4)$$

(where  $\mu_T$  is the total ionic strength,  $\mu_1$  is the ionic strength of the electrolyte whose activity coefficient is  $\gamma$ ,  $\mu_0$  is the formula weight of solvent,  $m_T$  the total molality, and  $u$ ,  $A$ ,  $B$ , and  $B'$  are constants), may be employed to calculate  $\gamma$  for all these solutions if the  $A$ ,  $B$ , and  $B'$  constants are varied arbitrarily.<sup>3</sup>

(6) For uniunivalent electrolytes at constant total molality, the above equation reduces to

$$\log \gamma = a'c + \text{constant} \quad (5)$$

where  $a'$  is a constant. It has been shown that this simple relation is valid within very narrow limits up to total concentrations as high as 3M for

<sup>1</sup> Harned, *J. Amer. Chem. Soc.*, **38**, 1986 (1916); **42**, 1808 (1920); **48**, 326 (1926); Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922); Åkerlöf, *ibid.*, **48**, 1160 (1926).

<sup>2</sup> Hückel, *Physik. Z.*, **26**, 93 (1925).

<sup>3</sup> Harned and Åkerlöf, *Physikal. Z.*, **27**, 411 (1926).

hydrochloric acid in halide solutions.<sup>4</sup> More recently, Güntelberg has shown the exactness of this law to be within  $\pm 0.04$  per cent. at 0.1 total concentration.<sup>5</sup> The validity of this law is of great value, since it permits us to compute the activity coefficient of hydrochloric acid at zero concentration in a chloride solution of concentration  $m$ . Thus, if we know the activity coefficient of the chloride ion in such a solution, we may compute the activity coefficient of the hydrogen ion. This would be equal to  $\gamma_H$  in a pure aqueous solution of the salt at that concentration, or  $\gamma_H$  in equation (1).

## (2) The Activity Coefficients of Strong Hydroxides in Homocationic Salt Solutions.

The electromotive forces of the cells :



are given by the equation,<sup>6</sup>

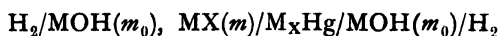
$$E + 0.05915 \log \frac{p_2}{p_1} = 0.1183 \log \frac{\gamma_2 m_2}{\gamma_1 m_1} \quad (6)$$

where  $p_2, p_1$  are the vapour pressures of the solutions, and  $\gamma_2, \gamma_1$  are the activity coefficients of the hydroxide in the solutions of molal concentrations  $m_2$  and  $m_1$  respectively. From these measurements, we find that

$$\gamma_{KOH} > \gamma_{NaOH} > \gamma_{LiOH}$$

at a given concentration, which is just the opposite to the behaviour of the halides. This cannot be accounted for by Hückel's theory,<sup>2</sup> or by an hydration theory such as the one of Bjerrum.<sup>7</sup>

The activity coefficients of these hydroxides in halide solutions may be obtained from measurements of the cells :



by the equation,<sup>8</sup>

$$E_2 = 0.05915 \log \frac{\gamma_{M(S)}\gamma_{OH(S)}a_{H_2O(m_0)}(m + m_0)m_0}{\gamma_{M(m_0)}\gamma_{OH(m_0)}a_{H_2O(S)}m_0^2} \quad (7)$$

The properties of these hydroxides in the salt solutions are in sharp contrast to those of the acids in the same solutions.

(1) At a given hydroxide and total concentration, the activity coefficients of these strong hydroxides are less in the solution of the salt of a given valence type which in the pure solvent possesses the higher activity coefficient.

Thus

$$\gamma_{KOH(KCl)} > \gamma_{NaOH(NaCl)} > \gamma_{LiOH(LiCl)}, \text{ and}$$

$$\gamma_{KOH(KCl)} > \gamma_{KOH(KBr)} > \gamma_{KOH(KI)},$$

while

$$\gamma_{LiCl} > \gamma_{NaCl} > \gamma_{KCl}, \text{ and}$$

$$\gamma_{KI} > \gamma_{KBr} > \gamma_{KCl}.$$

<sup>4</sup> Harned, *J. Amer. Chem. Soc.*, **48**, 326 (1926).

<sup>5</sup> Güntelberg, *Z. physikal. Chem.*, **123**, 199 (1926).

<sup>6</sup> Knobel, *J. Amer. Chem. Soc.*, **45**, 70 (1923); Harned, *ibid.*, **47**, 676 (1925); Harned and Swindells, *ibid.*, **48**, 126 (1926).

<sup>7</sup> Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

<sup>8</sup> Harned, *J. Amer. Chem. Soc.*, **47**, 684 (1925); **47**, 689 (1925); Åkerlöf, *ibid.*, **48**, 1160 (1926).

This is just the opposite to the behaviours of the strong acids in these salt solutions.

(2) This fact is not in accord with Hückel's theory nor can the activity coefficients of the hydroxides in salt solutions be calculated from the data on the individual electrolytes or *vice versa* by Hückel's equations. The activity coefficient is less in the solution of the greater electrical field strength, a fact which is the opposite to the theoretical prediction.

(3) The results may be calculated, however, by equation (4), if we assign arbitrary values to A, B, and B'.

(4) The most important numerical result is the validity of the law of the linear variation of the  $\log \gamma$  at constant total ionic strength for the activity coefficients of the hydroxides in chloride and sulphate solutions. This is interesting, since we find that this law which is characteristic of the dilute as well as the concentrated solutions is more general than any of the theories of the subject. It is also useful since we can evaluate  $\gamma_{\text{NaOH}(\text{NaCl})}$  etc., in a

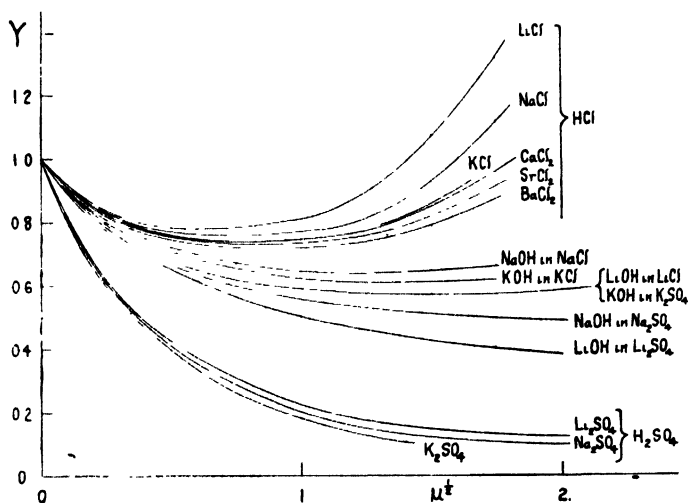


FIG. 1.—Activity Coefficients of Acids and Hydroxides in Salt Solutions.

solution containing the hydroxide at zero concentration, and, consequently, if we know the individual activity coefficient of the sodium ion in a sodium chloride solution of this strength, we may compute  $\gamma_{\text{OH}}$  in pure aqueous solution at this salt concentration, or  $\gamma_{\text{OH}}$  in equation (1).

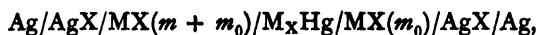
In Fig. 1, a graphical summary of the results of the activity coefficients of these acids and hydroxides at 0.1 *N* concentration in the salt solutions of varying concentration is given. These curves will suffice to show the sequence of results and to give a comparison of the behaviours of the acids and hydroxides.

### (3) The Ionic Activity Coefficient Product of, and the Dissociation of Water in Salt Solutions.

By adding equations (2) and (7), letting  $m_2$  equal  $m$ ,  $m_1$  equal  $m_0$ , and rearranging terms, we obtain

$$E_1 + E_2 = 0.05915 \log \frac{\gamma_{\text{M}(\text{S})} \gamma_{\text{X}(\text{S})} (m + m_0)^2}{\gamma_{\text{M}(\text{m}_0)} \gamma_{\text{X}(\text{m}_0)} m_0^2} + 0.05915 \log \frac{\gamma_{\text{H}(\text{S})} \gamma_{\text{OH}(\text{S})} a_{\text{H}_2\text{O}(\text{m}_0)}}{\gamma_{\text{H}(\text{m}_0)} \gamma_{\text{OH}(\text{m}_0)} a_{\text{H}_2\text{O}(\text{S})}} \quad (8)$$

The first member on the right of this equation equals the electromotive forces,  $E_3$ , of the cells,



and therefore

$$E_1 + E_2 - E_3 = 0.05915 \log \frac{\gamma_{\text{H}(\text{S})} \gamma_{\text{OH}(\text{S})}}{\gamma_{\text{H}(m_0)} \gamma_{\text{OH}(m_0)}} = 0.05915 \log \frac{K_{\gamma(\text{S})}}{K_{\gamma(m_0)}} \quad (9)$$

$$a_{\text{H}_2\text{O}(m_0)}$$

Thus, if we know the electromotive forces of the above three cells, we may compute  $K_{\gamma(\text{S})}$  from a knowledge of  $K_{\gamma(m_0)}$ .<sup>9</sup>  $K_{\gamma(\text{S})}$  is the ionic activity coefficient product of water in a salt solution and is  $\frac{\gamma_{\text{H}} \gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}}$  in equation (1).

This coefficient equals unity at zero salt concentration and  $K$ , the equi-

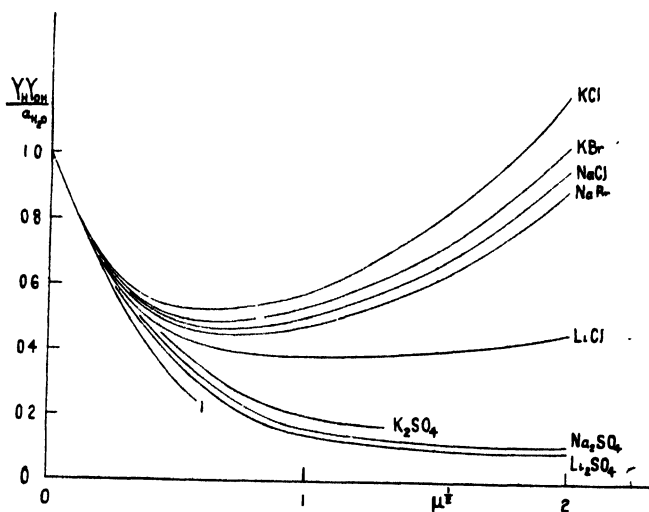


FIG. 2.—Ionic Activity Coefficient Product of Water in Salt Solutions.

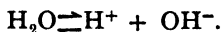
librium constant of equation (1) at zero salt concentration equals  $m_{\text{H}} m_{\text{OH}}$ , which is equal to  $1.005 \times 10^{-14}$  at  $25^\circ$ . Measurements of cells of these three types containing halides and sulphates, and acids and hydroxides at  $0.01\text{M}$  and  $0.1\text{M}$  are available. Results computed from the  $0.01\text{M}$  and  $0.1\text{M}$  series superimpose excellently. Although we have striven for an accuracy of  $\pm 0.1$  mv., the errors are greater than this in some cases and for this reason we have made no attempt to extrapolate the results to zero concentration. This will be done at a future time when the final results are at our disposal. So far we have calculated  $K_{\gamma(\text{S})}$  at  $0.01\text{M}$  by the use of the Debye and Hückel function. A summary of some of the results is given in Fig. 2. Curve 1 is that obtained by means of the limiting function of Debye and Hückel.

The sequence of results is interesting since the ionic activity coefficient product of water is always less in the solution of the salt which has the

<sup>9</sup> Harned, *J. Amer. Chem. Soc.*, **43**, 930 (1925); Harned and Swindells, *ibid.*, **48**, 126 (1926); Åkerlöf, *ibid.*, **48**, 1160 (1926); Harned and James, *J. physical Chem.*, **30**, 1060 (1926).

higher activity coefficient. This we have found to be the peculiarity of the hydroxide—salt solutions. Since according to equation (1),  $K_{\gamma(S)}$  times  $m_{H^+}m_{OH^-}$  is equal to  $1.005 \times 10^{-14}$  at  $25^\circ$ ,  $m_{H^+}m_{OH^-}$  or the dissociation of water is greater in the solution of the salt which has the higher activity coefficient.

There is one consideration which should be mentioned. Equation (1) is valid upon the assumption that the water dissociation takes place according to the tentative scheme



If, however, the dissociation is represented by



then  $K_{\gamma(S)}$  as above determined will equal  $\frac{\gamma_{H_3O^+}\gamma_{OH^-}}{a_{H_2O}^2}$ , the equilibrium constant will be given by

$$K = K_{\gamma(S)} m_{H_3O^+} m_{OH^-}$$

and, therefore, the method will measure  $m_{H_3O^+}m_{OH^-}$ . In any case, our method gives the product of the ionic species produced by the dissociation of water.

#### (4) On Individual Ionic Activities.

So far we have obtained a knowledge of the activity coefficient of a salt,  $\sqrt{\gamma_M\gamma_X}$ , in the pure solvent from which we may calculate  $a_{H_2O}$ . We have also evaluated  $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$  in the salt solutions from which we may compute  $m_{H^+}m_{OH^-}$ . We have also measured  $\gamma_{HX}$  in homoanionic salt solutions,  $\gamma_{MOH}$  in homocationic salt solutions. But since we have no reason to regard  $\gamma_H$  equal to  $\gamma_{OH^-}$  or  $\gamma_M$  equal to  $\gamma_X$ , or  $m_H$  equal to  $m_{OH^-}$  in a given salt solution, it is necessary to obtain some basis for the computation of these quantities.

The general thermodynamic equation which we may employ to define a liquid junction potential,  $E_b$ , may be written

$$E_b = - \sum \frac{RT}{nF} \int_1^2 t_i d \ln a_i \quad . \quad . \quad . \quad (10)$$

where  $t_i$  and  $a_i$  are the transference number and activity of an ion of the  $i$ th kind. This equation is not completely general since the relatively small term due to solvent transfer has been omitted. The summation is for all the ions and the integral is to be taken from solution 1 to solution 2 throughout the region of mixing. For univalent electrolytes, since  $a_i$  equals  $\gamma_i m_i$ , this equation becomes

$$E_b = - \sum 0.05915 \int_1^2 t_i d \log \gamma_i - \sum 0.05915 \int_1^2 t_i d \log m_i \quad . \quad (11)$$

The second member on the right of this equation is the integral used by Henderson.<sup>10</sup> To evaluate the first integral, the  $\gamma_i$ s must be known.

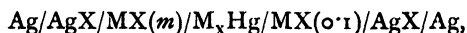
In evaluating activity coefficients, we always refer them to an arbitrary standard (e.g.,  $\gamma = 1$ , when  $m = 0$ ). To define an individual ionic activity coefficient from a purely thermodynamic point of view, it is also necessary to choose a standard state. Since it is impossible to remove an ion from a

<sup>10</sup> Henderson, *Z. physikal. Chem.*, **59**, 118 (1907); **63**, 325 (1908); Harned, *J. physical Chem.*, **30**, 433 (1926).

solution and measure the free energy change of such a process, it is necessary to refer all individual ionic activity coefficients to some ionic solution. Let that solution be potassium chloride, and let the arbitrary state for all individual ion activities be the condition that at all concentrations the activity coefficients of the potassium and chloride ions are the same. In other contributions to this subject, this has been regarded as a postulate depending on the speculation that since the electronic structure, the mobilities, hydration values, etc., of these ions are so nearly the same, their activity coefficients would be identical.

This definition has obvious advantages. Since the transference numbers of the potassium and chloride ions are nearly the same and, since we make  $\gamma_K$  equal to  $\gamma_{Cl}$ , it is obvious from equation (11) that when the transference is to a large extent by the potassium and chloride ions,  $E_t$  will be small. Thus, a potassium chloride bridge will reduce  $E_t$  to a very small value, but this is only true when  $\gamma_K$  and  $\gamma_{Cl}$  are defined as being equal.

As a second step towards a solution of this problem, MacInnes<sup>11</sup> stated that in a chloride solution of a given strength and of a given valence type, the activity coefficient of the chloride ion is the same, independent of the nature of the cation. This is equivalent to the statement that the electromotive forces,  $E_{\pm}$ , of the potassium, sodium, lithium, and chloride ions are additive, or that the electromotive forces of the cells,



referred to a given concentration (*e.g.* 0.1M) should show additive properties.<sup>12</sup> Recently, we have been making a very careful investigation of cells of this type containing concentrated solutions and find that the electromotive forces of the chlorides, bromides, and iodides of the alkali metals and hydrogen are approximately additive even up to concentrations as high as 3M. The departure from additivity is of the order of tenths of millivolts. This holds approximately only for the ions of the noble gas type structure. It does not hold for the nitrate, iodate, etc., ions of more complex structure nor for the hydroxide, formate, and cyanide ions of the far less symmetrical structure.

If we are permitted to employ the above definition and the principle of additivity, or some principle which departs little from additivity, we can compute  $\gamma_M$ ,  $\gamma_X$ , and by the use of the law of the linear variation of  $\log \gamma$  we may calculate  $\gamma_H$  and  $\gamma_{OH}$  in the pure aqueous halide solutions. We may also compute the latter in acid-halide and hydroxide-halide solutions. We have shown that  $m_H m_{OH}$  may be calculated, but a method of determining  $m_H$  or  $m_{OH}$  individually has not been developed.

### (5) One Aspect of the Behaviours of Symmetrical and Unsymmetrical Ions.

The most striking feature of these results is the contrast between the acid-salt and hydroxide salt systems, or between the hydrogen and hydroxyl ion activity coefficients in the halide solutions. Thus,

$$\begin{array}{l} \text{while} \quad \gamma_{H(LiCl)} > \gamma_{H(NaCl)} > \gamma_{H(KCl)} \\ \text{Further} \quad \gamma_{OH(LiCl)} < \gamma_{OH(NaCl)} < \gamma_{OH(KCl)}. \\ \gamma_{H(LiCl)} > \gamma_{OH(LiCl)}; \gamma_{H(NaCl)} > \gamma_{OH(NaCl)}; \text{ etc.} \end{array}$$

<sup>11</sup> MacInnes, *J. Amer. Chem. Soc.*, **41**, 1086 (1919).

<sup>12</sup> Harned, *J. physical Chem.*, **30**, 433 (1926); Douglas, Thesis, University of Pennsylvania (1926); Harned and Douglas, *J. Amer. Chem. Soc.*, **48**, 3095 (1926).

If we make the assumption which results from Hückel's theory that the greater the activity coefficient of a halide at a given concentration, the greater the electrical field strength of its solution, we may then state that in a halide solution, the hydrogen ion activity coefficient is greater, and the hydroxyl ion activity coefficient is less, in the solution which at a given concentration possesses the highest electrical field intensity. As we have pointed out, this behaviour of the hydrogen ion is not contrary to a theory such as Hückel's, but the behaviour of the hydroxyl ion is just the opposite to what we deduce from this theory.

If we adopt this point of view, we are in contact with an interesting example of the effect of the electrical field of a solution on the activity coefficient of ions. Perhaps a glimmer of truth may be obtained by a general consideration of the problem of electrical interaction of ions in its relation to the kind of ion. Brönsted<sup>13</sup> and more recently Bjerrum<sup>14</sup> have considered the possibility of interaction of ions of opposite sign to form associated ionic complexes. It does seem probable that such an interaction would be likely to occur in some cases and to some extent. Since, however, the partial free energies of the ions of the electronic structure of the rare gas type are so nearly additive, it does not seem probable that much interaction takes place among them. It would seem that electrical interaction between ions will depend more on the kind than the size of the ion and to be a more complicated process than the formation of simple electrically neutral complexes.

Let us consider the departure from the behaviour of the simplest and most symmetrical rare gas type ions upon substituting a more complex and more unsymmetrical anion. We find that at a given concentration,

$$\gamma_{\text{NaCl}} > \gamma_{\text{KCl}}; \gamma_{\text{NaIO}_3} = \gamma_{\text{KIO}_3}; \gamma_{\text{NaOH}} < \gamma_{\text{KOH}}$$

The properties of the nitrate and sulphate ions which are complex but symmetrical lie between those of the chlorides and iodates. The hydroxyl ion is highly unsymmetrical and, therefore, will be more easily deformed by the electrical field, and the extent of deformation will be greater the greater the field intensity. Thus, in the presence of the lithium ion or a lithium salt, the hydroxyl ion is less symmetrical than in the presence of the potassium ion or a potassium salt. Since ions of less symmetry have the lower activity coefficients, this is in the expected direction. If this is the case, then the cyanide ion should act similarly to the hydroxide ion. This seems to be true both from its catalytic behaviour in neutral salt solutions and from its thermodynamic properties. Recently,<sup>15</sup> from velocity measurements of the hydrolysis of ethyl formate, an approximate calculation of the activity coefficient of formic acid in some salt solutions has been made. It was found that its activity coefficient is less in the solution of a given strength of that electrolyte of a given valence type which possesses the higher activity coefficient. Thus, the unsymmetrical formate ion acts similarly to the hydroxyl ion.

### Summary.

(1) A discussion of the thermodynamic properties of acids and hydroxides in salt solutions has been given. The properties of the acid-salt systems have been contrasted with those of the hydroxide-salt systems.

<sup>13</sup> Brönsted, *J. Amer. Chem. Soc.*, **44**, 877 (1922).

<sup>14</sup> Bjerrum, *Det. Kgl. Danske Videnskabernes Selskab.*, **7**, 9 (1926).

<sup>15</sup> Harned, *J. Amer. Chem. Soc.*, **49**, 1 (1927).

(2) The method for and the results of the determination of the ionic activity coefficient product and dissociation of water in some salt solutions have been presented.

(3) A thermodynamic definition of individual ion activity has been given, and a means for the evaluation of the individual ion activity coefficients of some simple electrolytes and mixtures has been discussed.

(4) A suggestion which may help to explain the peculiarities of some unsymmetrical ions has been made.

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## AN ELECTROMETRIC STUDY OF THE SYSTEM POTASSIUM CHLORIDE — LEAD CHLORIDE — WATER AT 25° C.

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(Received 30th March, 1927.)

One of the authors recently published<sup>1</sup> the results of an investigation of the equilibria existing at 25° C. in systems consisting of a lead halide, the corresponding potassium halide, and water. In the chloride system, in addition to the two simple chlorides, two other solid phases were present, *viz.*,  $2\text{PbCl}_2$ ,  $\text{KCl}$  and  $\text{PbCl}_2$ ,  $\text{KCl}$ ,  $\frac{1}{3}\text{H}_2\text{O}$ . In this respect, his results agreed with those of Brönsted<sup>2</sup> and also with those of Demassieux,<sup>3</sup> the latter of which appeared after his own experiments had been commenced. On the other hand, they were in marked disagreement with recent work of Kendall and Sloan,<sup>4</sup> who, amongst other points of difference, found the second double salt mentioned to be anhydrous. His results are shown in Fig. 1, which is self-explanatory.

During the course of the work, it became obvious that the system was one which, from certain points of view, was particularly adapted for thermodynamic study, and the measurements were taken in hand. The present paper contains an outline of the methods and results; a fuller and supplementary account will appear elsewhere.

In any solution of the components capable of existence at 25°, let  $N_1N_2N_3$  represent the molar fractions of  $\text{PbCl}_2$ ,  $\text{KCl}$  and  $\text{H}_2\text{O}$  respectively, and  $a_1a_2a_3$  their activities. In each case, the standard state of activity is chosen as being that of the pure substance. As far as water is concerned, this corresponds to the common practice. On the other hand, it is usual to refer the activity of solutes to a standard state defined in such a way that  $a/N$  is unity when  $N$  is zero. In view, however, of the facts (1) that the course of the activity coefficient-concentration curve for  $\text{PbCl}_2$  in dilute solutions is not well known, (2) that most of the solutions investigated were far from dilute as far as  $\text{KCl}$  was concerned, (3) that the activities of the saturated solutions were to play an important part in our deductions, we thought it better to depart from the usual procedure and to express our results as stated above.  $a_1$  and  $a_2$  will therefore be *unity for solutions in*

<sup>1</sup> L. J. Burrage, *J. Chem. Soc.*, 1926, 1703.

<sup>2</sup> *Z. physikal. Chem.*, 1912, 80, 206.

<sup>4</sup> *J. Amer. Chem. Soc.*, 1925, 47, 2306.

<sup>3</sup> *Ann. Chimie.*, 1923, 20, 233.

equilibrium with solid lead chloride and potassium chloride respectively and will be less than unity for all other solutions.

Referring now to Fig. 1, we see that, for solutions of compositions

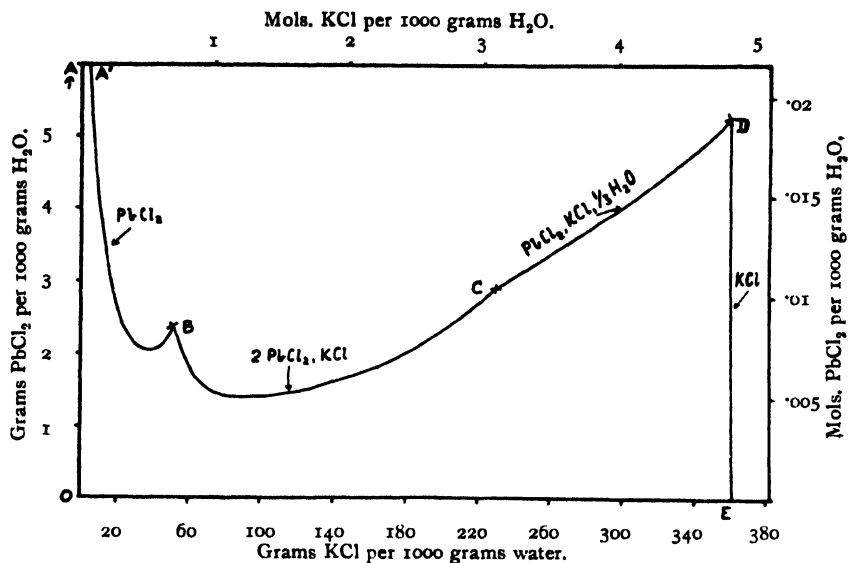


FIG. 1.

corresponding to various lines drawn on the diagram, certain relations obviously hold, and certain others can be deduced by means of the Gibbs' partial molal free energy equation,

$$N_1 \cdot d \ln a_1 + N_2 \cdot d \ln a_2 + N_3 \cdot d \ln a_3 = 0.$$

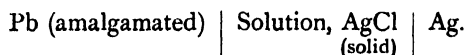
These are expressed in the following table:—

TABLE I.

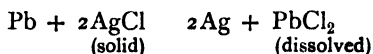
Line or Curve.	Defining Conditions.	Relation following on Application of Gibbs' Equation.
OA . . . . .	$N_2 = 0; a_2 = 0.$	$\int d \ln a_1 = - \int \frac{N_3}{N_1} \cdot d \ln a_3.$
OE . . . . .	$N_1 = 0; a_1 = 0.$	$\int d \ln a_2 = - \int \frac{N_3}{N_2} \cdot d \ln a_3.$
Any horizontal line . . . . .	$\frac{N_1}{N_3}$ constant.	
Any vertical line . . . . .	$\frac{N_2}{N_3}$ constant.	
Any straight line passing through O, other than OA and OE.	$\frac{N_1}{N_2}$ constant.	
A'B . . . . .	$a_1 = 1.$	$\int d \ln a_2 = - \int \frac{N_3}{N_2} \cdot d \ln a_3.$
BC . . . . .	$a_1^2 \cdot a_2 = \text{constant}.$	$\int d \ln a_3 = \int \frac{2N_2 - N_1}{N_3} \cdot d \ln a_1.$
CD . . . . .	$a_1 \cdot a_2 \cdot a_3^{\frac{1}{2}} = \text{constant}.$	$\int d \ln a_3 = \int \frac{3(N_2 - N_1)}{3N_3 - N_2} \cdot d \ln a_1.$
DE . . . . .	$a_2 = 1.$	$\int d \ln a_3 = - \int \frac{N_1}{N_3} \cdot d \ln a_1.$

**Experimental.**

Our experiments have been designed to utilise the above relations. So far, no aqueous vapour pressure measurements, which, from the relation  $a_3 = p/p_0$ , would give us  $a_3$  values directly, have been carried out, as the general activity relations for the greater part of the system could be mapped out in some detail without them. They are, however, essential for the treatment of the concentration field lying under AB, and will, it is hoped, shortly be undertaken. The method recently described by Pearce and Snow<sup>5</sup> promises to be sufficiently accurate for our purpose. All  $a_3$  and  $p$  values quoted, with the exception of those for pure KCl solutions, are therefore calculated figures. Nor have  $a_2$  values been determined directly, and indeed we cannot see how this could be done in presence of the dissolved  $\text{PbCl}_2$ . A systematic study has been made, on the other hand, of  $a_1$ . This has been done by studying the cell,



The cell reaction along OA, DE, and in the whole interior of the diagram is



and the differences in *E.M.F.* found will depend solely on differences in  $a_1$ . If  $a_1$  is the  $\text{PbCl}_2$  activity and  $E_1$  the measured *E.M.F.* of any cell of this type, whilst  $E_0$  is the *E.M.F.* of a similar cell in which, however, solid (not dissolved)  $\text{PbCl}_2$  is produced, then, as by definition  $a_1 = 1$  for solutions in equilibrium with solid  $\text{PbCl}_2$ , we have

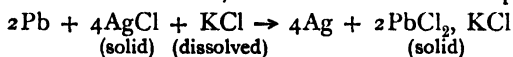
$$E_0 - E_1 = 0.02957 \log a_1. \quad (1)$$

Cells with *E.M.F.* =  $E_0$  are those in which the electrolyte is of composition corresponding to points on A'B, and their common *E.M.F.*, the mean of a large number of closely agreeing readings, is 0.4837 volt.

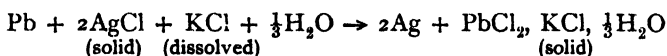
Hence

$$\log a_1 = \frac{0.4837 - E_1}{0.02957}. \quad (2)$$

Along the curves BC and CD, the cell reactions are respectively



and



Differences in  $E_1$  will thus depend solely on differences in  $a_2$  and in  $a_3$  respectively. In virtue, however, of the relations between  $a_1$ ,  $a_2$  and  $a_3$  holding along BC and CD (see column 2 of Table I.), it is clear that, as before, the values of  $a_1$  for the corresponding solutions are given by equation (2).

With regard to the experimental details, a few points may be noted. The electrodes of pure lead were amalgamated and gave more reproducible figures than some which had been lead-plated. In our first measurements, we used Hg/HgCl electrodes instead of Ag/AgCl electrodes. The results obtained were reproducible enough, but work was slow. On the suggestion of Mr. Wolfenden, of the Balliol and Trinity Laboratories, Oxford, we changed over to the Ag/AgCl electrodes and greatly increased our rate of work.

The silver electrodes were electrodeposited on to Pt wires, and then chloridised anodically. They gave excellent results. In the majority of cases, the lead and silver electrodes were contained in separate vessels, but with solutions free from KCl, and therefore of low conductivity, the two electrodes were in close proximity in the same vessel. Certain disturbing effects were encountered. The most important was that due to small amounts of dissolved oxygen attacking the lead electrode. In solutions containing little  $\text{PbCl}_2$ , it was necessary to displace all air beforehand by a stream of purified nitrogen; we think that our measurements with very dilute KCl-free,  $\text{PbCl}_2$  solutions, which were not reproducible, were affected by traces of residual oxygen. Another difficulty met with in solutions more concentrated than 3 N. KCl was the appreciable solubility of AgCl. *E.M.F.* variations disappeared after the electrolyte had dissolved a certain amount of AgCl, and we do not think that the  $\text{Cl}^-$  ion activity was appreciably affected thereby. Precautions were taken which effectually prevented any diffusion of the dissolved AgCl to the lead electrode. All the electrolytes were made up by weight at least in duplicate and, in every case, readings taken with at least two different lead and two different chloridised silver electrodes. We estimate the error of the final values given, in the great majority of cases, to be less than 0.0002 volt and, indeed, usually under 0.0001 volt.

### Results.

In order that the *E.M.F.* of any cell containing an unsaturated solution might serve the double purpose of illustrating the variation of  $a_1$  both with constant  $\frac{N_1}{N_3}$  and variable  $\frac{N_2}{N_3}$ , and with constant  $\frac{N_2}{N_3}$  and variable  $\frac{N_1}{N_3}$ , all unsaturated electrolytes were made up to one of a definite limited number of  $\frac{N_1}{N_3}$  ratios and simultaneously to one of a definite limited number of  $\frac{N_2}{N_3}$  ratios. Expressed in grams per 1000 grams of water, the weights of  $\text{PbCl}_2$  taken were 0.125, 0.25, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0, whilst the weights of KCl were 3.75, 7.5, 15, 35, 52, 68, 90, 130, 170, 231, 292 and 330. In this way 65 experimental points were determined. In addition, readings were made for these concentrations on the series of curves A'B to DE which corresponded to the same  $\frac{N_1}{N_3}$  or  $\frac{N_2}{N_3}$  ratios, and 24 more experimental points were thus obtained. Finally, some 18 different concentrations of  $\text{PbCl}_2$  solutions, free from KCl, were measured. These will not be discussed further here, for the reason already given.

The results obtained were then plotted in various ways:—

- (i) E against grams KCl/1000 grams water—for the curves BC and CD.
- (ii) E against grams KCl/1000 grams water—for various constant values of grams  $\text{PbCl}_2$ /1000 grams water.
- (iii) E against grams  $\text{PbCl}_2$ /1000 grams water—for various constant values KCl/1000 grams water.
- (iv) E against the logarithm of grams  $\text{PbCl}_2$ /1000 grams water for various constant values of grams KCl/1000 grams water.

From these sets of curves were read off  $\text{PbCl}_2$  and KCl concentration figures corresponding to certain definite values of E, which, in their turn, corresponded to definite fractional values of  $a_1$ . The  $a_1$  and E values are contained in the following table:—

TABLE II.

E.	$a_1$ .
0.4875 volt	0.75
0.4926 "	0.5
0.5044 "	0.2
0.5133 "	0.1
0.5222 "	0.05
0.5340 "	0.02
0.5428 "	0.01

By means of the  $[\text{KCl}]$  and  $[\text{PbCl}_2]$  figures thus obtained, the broken curves in Fig. 2 were drawn. Together with A'B, they constitute a series of curves along each of which  $a_1$  is constant at some definite figure. For such curves we suggest the name of *isodynes*.

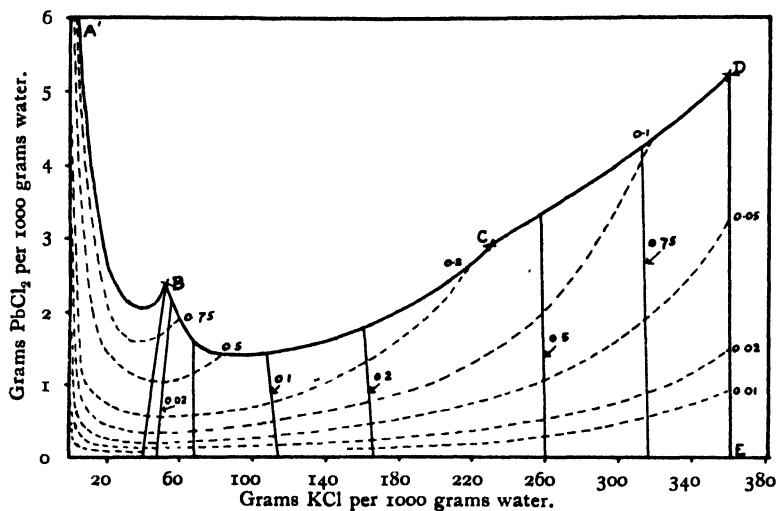


FIG 2.

We then proceeded as follows:

(1) By extrapolation of the vapour pressure measurements made by Lovelace, Frazer and Sease<sup>6</sup> on potassium chloride at  $20^\circ$  to a molecular concentration of 4.84, corresponding to point E on the diagram, we obtained a figure of 14.782 mm. (This solution would of course actually be *super-saturated* in practice.) Taking  $p_0$  at  $20^\circ$  as 17.539 mm.,  $a_3$  for this solution at  $20^\circ$  becomes 0.842(8). We assumed that the same value of  $a_3$  would hold for the same solution at  $25^\circ$ , now a saturated one. The figure taken from the recent data for this temperature obtained by Pearce and Snow<sup>6</sup> is practically identical.

(2) Along DE,  $d \ln a_2 = 0$ . Hence

$$\int d \ln a_3 = - \int \frac{N_1}{N_3} \cdot d \ln a_1.$$

Sufficient values of  $a_1$  are available to make the graphical integration possible. Carrying this out, we obtained for  $a_3$  at D the figure 0.842(4). The small quantity of dissolved  $\text{PbCl}_2$  (5.27 grams/1000 grams  $\text{H}_2\text{O}$ ) makes a hardly perceptible difference.

<sup>6</sup> *J. Amer. Chem. Soc.*, 1921, 43, 102.

(3) Utilising this figure for  $a_3$  at D, the known variation of  $a_1$  along CD, and the equation  $\int \mathrm{d} \ln a_3 = \int \frac{3(N_2 - N_1)}{3N_3 - N_2} \cdot \mathrm{d} \ln a_1$  (see Table I.), we obtained by graphical integration, the values of  $a_3$  at different points along CD. At the transition point C,  $a_3$  is 0.897(8).

(4) Knowing that, at D,  $a_1 = 0.0783$ ,  $a_2 = 1$ , and  $a_3 = 0.842(4)$ , we get that

$$\log a_1 + \log a_2 + \frac{1}{3} \log a_3 = 2.8692.$$

This is constant along CD, and hence  $a_2$  can be calculated for any point on the curve. At C it is 0.403.

(5) Knowing that, along BC, the product  $a_1^2 \cdot a_2$ , and therefore the sum  $2 \log a_1 + \log a_2$ , are both constant, and that, from the figures at the point C, this last sum is 2.1644—knowing, in addition, the value of  $a_1$  at any point along BC, the corresponding value of  $a_2$  can be calculated. At B,  $a_2$  is 0.0146.

(6) Making use of the relation  $\int \mathrm{d} \ln a_3 = \int \frac{2N_2 - N_1}{N_3} \cdot \mathrm{d} \ln a_1$ , the values of  $a_3$  were calculated for points along BC. At B,  $a_3$  was found to be 0.980(4). To check the graphical integration, the process was repeated, using the expression,

$$\int \mathrm{d} \ln a_3 = - \int \frac{N_2}{N_3} \cdot \mathrm{d} \ln a_2 - \int \frac{N_1}{N_3} \cdot \mathrm{d} \ln a_1.$$

The result was practically identical.

(7) Making the assumption already used under (1)—*viz.* that, for any weight molal KCl solution,  $a_3$  at 25° is the same as at 20°, as given by the figures of Lovelace, Frazer and Sease, the values of  $a_2$  at any concentration along OE can be calculated by application of the equation,

$$\int \mathrm{d} \ln a_2 = - \int \frac{N_3}{N_2} \cdot \mathrm{d} \ln a_3.$$

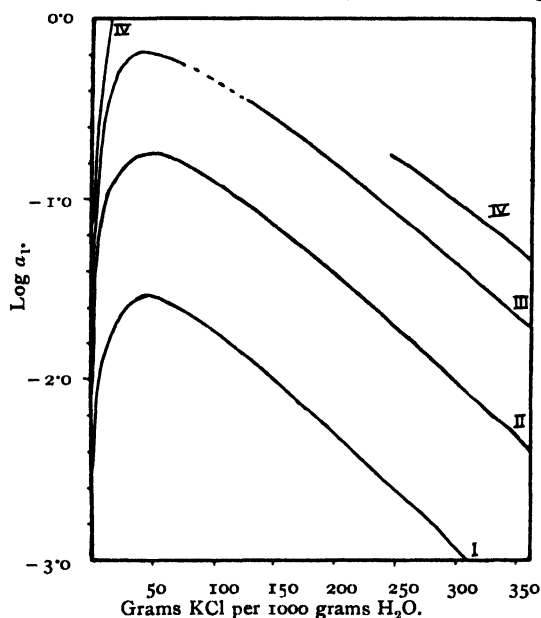
Points representing (i) solutions along OE, (ii) solutions along BC - CD with identical values of  $a_2$  have been provisionally joined by straight lines. If the correctness of the experimental work and deductions could be relied on, these would probably represent KCl isodynes, although, in default of vapour pressure measurements made on the solutions whose compositions lie along them, this cannot be stated with certainty. The fact, however, that DE ( $a_2 = 1$ ) is practically rectilinear suggests that this may be also true of other KCl isodynes.

Whether or not these pairs of points joined up in this fashion really represent solutions with identical  $a_2$  values can be checked in a simple way—*viz.*, by use of the equation,

$$\int \mathrm{d} \ln a_2 = - \int \frac{N_1}{N_2} \cdot \mathrm{d} \ln a_1 - \int \frac{N_3}{N_2} \cdot \mathrm{d} \ln a_3.$$

If all is in order, the right hand side of the equation should be zero. A particularly simple case is furnished by the solutions containing 68 grams KCl/1000 grams water, where not only (presumably) the  $a_2$  values, but also the  $\frac{N_1}{N_3}$  ratios are identical. As the first term on the right-hand side is very small (it can be evaluated with sufficient accuracy by graphical integration), it follows that  $\mathrm{d} \log a_3$  should be nearly zero, *i.e.* that the two solutions should have practically the same  $a_3$  values, or aqueous vapour pressures

We found that this was *not* so; the calculated figure of  $a_3$  for the solution



Curve I. 0.125 grams PbCl<sub>2</sub> per 1000 grams H<sub>2</sub>O.  
 " II. 0.5 " " " "  
 " III. 1.5 " " " "  
 " IV. 4 " " " "

FIG. 3.

for solutions along the curves BC - CD behave as if they were a little too low; or, alternatively if they be correct, the calculated  $a_3$  values along the same curves are too low. This error, whatever its cause, is greatest between B and about 100 grams KCl/1000 grams H<sub>2</sub>O (*i.e.* around the bend of the curve) and rapidly decreases as the concentration increases. Thus, expressed as a vapour pressure error, it corresponds to 0.06 mm. at B and to 0.08 mm. at 68 grams KCl/1000 grams H<sub>2</sub>O, but only to 0.01 - 0.02 mm. at C and at higher concentrations. It is difficult at the moment to discuss its cause or causes, and we prefer to wait until the necessary vapour pressure measurements have been done. In any case, the general nature of the KCl isodynes will be as shown, although it may well be possible that the vertical member of the series may correspond to a lower KCl concentration than actually shown, those lying to the right of it in the diagram being less steep, those on the left more steep, than actually drawn.

containing PbCl<sub>2</sub> was 0.967, for the solution without PbCl<sub>2</sub> 0.971, corresponding to vapour pressures of 16.95 and 17.03 mm. respectively. On the other hand, at a concentration of about 56 grams KCl/1000 grams water, the vapour pressures of the solutions with and without PbCl<sub>2</sub> are identical and the values of  $a_2$  differ appreciably. Further investigation showed that a slight error of this description persisted all through that part of the system dealt with, *i.e.* that portion lying to the right of the KCl isodyne drawn through B. Assuming the correctness of the  $a_3$  values for pure KCl solutions and of the  $a_2$  values calculated from them, the  $a_3$  values

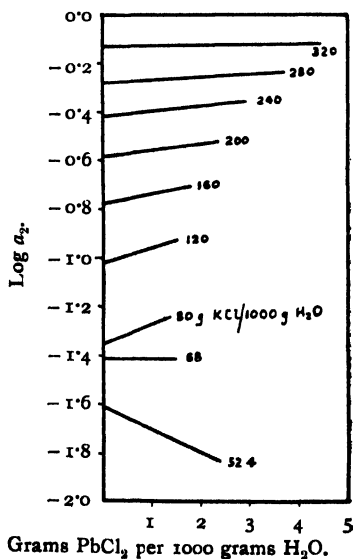


FIG. 4.

We do not propose in this paper to go into any detail with regard to the various relations which can be deduced between the  $m$ ,  $a$  and  $\gamma$  values for the dissolved  $\text{PbCl}_2$ ,  $\text{KCl}$  and their ions. Such a discussion will be more fruitful when more accurate measurements (which are now being carried out) on the behaviour of  $\text{PbCl}_2$  solutions, free from  $\text{KCl}$ , are available. The general nature of the effects of continuous addition of  $\text{KCl}$  on the  $a_1$  values of a solution with constant  $\frac{N_1}{N_3}$  ratio, and of  $\text{PbCl}_2$  on the  $a_2$  values of a solution with constant ratio  $\frac{N_2}{N_3}$  are, however shown in Figs. 3 and 4.

The lead chloride activity of a solution of constant lead chloride molality is at first increased by  $\text{KCl}$  addition and then decreased. The value of  $\text{KCl}$  at which  $a_1$  becomes a maximum is seen to vary slightly between the limits of about 35-45 grams  $\text{KCl}/1000$  grams  $\text{H}_2\text{O}$ . The nature of the effect on  $a_2$  of adding  $\text{PbCl}_2$  to a  $\text{KCl}$  solution (the course of the curve is provisionally taken as being linear) is seen to depend essentially on the molality of the  $\text{KCl}$ —a decrease when this is low, becoming less pronounced as  $\frac{N_2}{N_3}$  becomes greater, changing over to an increase and this, in turn, becoming less pronounced as the state of saturation with  $\text{KCl}$  is approached. In both cases we appear to be dealing with more than one concurrent effect. Their further analysis will be deferred.

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## A NOTE ON THE OCCURRENCE OF POINTS OF INFLEXION IN THE CONCENTRATION-VAPOUR PRESSURE CURVES OF AQUEOUS SOLUTIONS OF CERTAIN ELECTROLYTES.

BY A. J. ALLMAND.

(Received 24th March, 1927.)

### Introductory.

Work carried out in recent years on the vapour pressures of aqueous solutions of strong electrolytes has revealed the existence of irregularities in the curves connecting molecular lowering of vapour pressure and weight concentration. Such is the case with  $\text{KCl}$  at  $20^\circ$ ,<sup>1</sup> and at  $25^\circ$ ,<sup>2</sup> where the curves show minima, and with  $\text{LiCl}$  at  $20^\circ$ ,<sup>3</sup> where points of inflexion exist (together with an obvious minimum at very low concentrations). In addition, if the work of Bousfield and Bousfield<sup>4</sup> on  $\text{NaCl}$  solutions at  $18^\circ$  be calculated in this way, a well-marked minimum is found in the plot. Lovelace, Frazer, and their co-workers are quite clear that the irregularities are real, and not attributable to experimental error. The main features of the  $\frac{p_0 - p}{m}$  curves they ascribe to hydration effects, and the minor irregularities to a change in the state of molecular aggregation of the water. Pearce and Snow, whose published results are of a slightly lower order of

accuracy, are definite about the existence of a minimum in the KCl curve, but do not claim to be able to analyse the latter in greater detail.

Closely bound up with the presence of these irregularities is the fact that the corresponding vapour pressure-weight concentration curves show points of inflexion. This, in its turn, is connected with the existence of marked minima in the activity coefficient-concentration curves for these electrolytes. Such minima imply that the activity-concentration curves will show corresponding points of inflexion, and this means that points of inflexion will occur in the vapour pressure—concentration curves, calculable by applying the Gibbs' partial molal free energy equation to the equation connecting activity and concentration, if this is known. In default of any satisfactory equation, founded on theory, which expresses this last relation over the whole concentration range, recourse can be had to the Harned empirical equation,<sup>5</sup>

$$\log \gamma = am - \beta m^{a'}. \quad (1)$$

where  $\gamma$  and  $m$  have their usual significance, and  $a$ ,  $\beta$  and  $a'$  are constants characteristic of the electrolyte, having the following values<sup>6</sup> at 25°.

TABLE I.

	$a$ .	$\beta$ .	$a'$ .
KCl . .	0.07	0.292	0.396
NaCl . .	0.10	0.286	0.407
LiCl . .	0.21	0.323	0.463

### Calculation of Points of Inflexion in the $p/m$ Curves.

As the electrolytes considered are all binary, we have

$$\text{activity of electrolyte} = a_2 = m^2 \gamma^2. \quad (2)$$

Introducing the Gibbs' equation,

$$N_1 \cdot d \ln a_1 + N_2 \cdot d \ln a_2 = 0 \quad (3)$$

where  $N_1$  and  $N_2$  are the molar fractions of water and of the salt respectively, and  $a_1$ , the activity of the water, is  $p/p_0$ , we have

$$d \ln p = - \frac{2N_2}{N_1} \cdot d \ln(m\gamma) \quad (4)$$

and

$$\frac{dp}{dm} = - \frac{2N_2}{N_1} \cdot \frac{p}{m\gamma} \cdot \frac{d(m\gamma)}{dm} \quad (5)$$

From (1), we have

$$\frac{d(m\gamma)}{dm} = \gamma(1 + am - a'\beta m^{a'}) \quad (6)$$

Substituting, and replacing  $\frac{N_2}{N_1}$  by  $\frac{m}{55.5}$ , we get

$$\frac{dp}{dm} = - \frac{2p}{55.5} (1 + am - a'\beta m^{a'}) \quad (7)$$

Differentiating a second time, and equating  $\frac{a^2 p}{dm^2}$  to zero, we get, as the condition for the point of inflexion,

$$a - a'^2 \beta m^{a'-1} = \frac{2}{55.5} (1 + am - a'\beta m^{a'})^2 \quad (8)$$

Substituting the values of the coefficients given in Table I., we calculate as the concentrations for the points of inflexion the values in the second column of Table II. In the third column are put the observed values for these concentrations, read off as carefully as possible from plots of the experimental results.

TABLE II.

	Calculated for 25°.	Observed.
KCl . . . . .	1.475 <i>n</i>	{ 0.8 <i>n</i> (at 20°) 1 - 1.5 <i>n</i> at (25°) 1 <i>n</i> (at 18°) 0.35 - 0.4 <i>n</i> (at 20°)
NaCl . . . . .	0.58 <i>n</i>	
LiCl . . . . .	0.175 <i>n</i>	

The agreement is by no means good.

### Calculation of Minima in $\frac{p_0 - p}{m}$ Curves.

We have

$$\begin{aligned} \frac{d}{dm} \left( \frac{p_0 - p}{m} \right) &= -\frac{1}{m} \cdot \frac{dp}{dm} - \frac{p_0 - p}{m^2} \quad \quad \quad (9) \\ &= \frac{2}{55.5} \cdot \frac{p}{m} (1 + am - a' \beta m^{a'}) - \frac{p_0 - p}{m^2} \quad [\text{from (7)}] \end{aligned}$$

Whence, as condition for the minimum,

$$p_0 - p = \frac{2}{55.5} \frac{pm}{m} (1 + am - a' \beta m^{a'}) \quad \quad \quad (10)$$

This gives us the calculated figures in the second column of Table III. The third column contains the experimental values. Again the agreement is seen to be poor.

TABLE III.

	Calculated for 25°.	Observed.
KCl . . . . .	< 0.01 <i>n</i>	{ (a) 0.45 <i>n</i> ; (b) 1 - 1.25 <i>n</i> (at 20°) 1 - 1.2 <i>n</i> (at 25°) 1.6 <i>n</i> (at 18°) < 0.1 <i>n</i> (at 20°)
NaCl . . . . .	1.07 <i>n</i>	
LiCl . . . . .	< 0.01 <i>n</i>	

### Discussion.

The considerable and irregular discrepancies between calculated and observed values may be due to insufficiently accurate vapour pressure data, or to the use, in the calculation, of incorrect functional relations between activity and concentration, or to both causes.

With regard to the vapour pressure data, those of Lovelace, Frazer and their colleagues, obtained by a very accurate differential method, are undoubtedly more exact than those so far obtained by Pearce and Snow's ingenious dynamic method. The figures of Bousfield and Bousfield would appear to be of value, but unfortunately there are an insufficient number of experimental points in the concentration range which interests us. This is, to a certain extent, generally true of the other available data, and the

reading off of the most probable points of inflexion on the  $p/m$  curves presents difficulties, not only on account of the small changes in slope involved, combined with this paucity of points, but also because of the existence of experimental errors which, though small in absolute amount, are sufficient to render the results uncertain.

It would also appear, however, that the Harned formula is not adequate for the present purpose. It is frankly empirical, and designed to cover a very large concentration range. In the course of the evaluation of the most suitable figures for  $\alpha$ , it becomes amply clear that these are not true constants. A comparatively small change in  $\alpha$  will considerably affect the calculated values of  $m$ . Moreover, it would appear likely that  $\alpha$  varies with temperature to a greater extent than the other constants, and Harned's values have here been applied to measurements at temperatures other than 25°. Most important, however, is the fact that the equations derived from the Harned empirical formula only give *one* minimum (or maximum) value for the  $\frac{p_0 - p}{m}/m$  curves, and *one* point of inflexion on the  $p/m$  curves, whereas the accurate work of Lovelace, Frazer, and their colleagues, shows the  $\frac{p_0 - p}{m}/m$  curve at 20° for KCl to have two minima (and a maximum), and that for LiCl to have two points of inflexion, in addition to a very sharp minimum below 0.1 *n*. Similarly, on the KCl  $p/m$  curve for 20°, in addition to the point of inflexion at about 0.8 *n*., there are indications of others near 0.3 and 0.4 *n*. It is obvious that the  $\gamma - m$  functional relation which is going to satisfy the experimental results will be more complex than the Harned equation.

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- <sup>3</sup> Lovelace, Bahlke, and Frazer, *J. Amer. Chem. Soc.*, 1923, **45**, 2930.
- <sup>4</sup> W. R. Bousfield and C. E. Bousfield, *Proc. Roy. Soc. A.*, 1923, **103**, 429.
- <sup>5</sup> Harned, *J. Amer. Chem. Soc.*, 1920, **42**, 1808.
- <sup>6</sup> Harned, Article in H. S. Taylor's *Physical Chemistry*, p. 747.

## THE ACTIVITY OF ZINC CHLORIDE IN CONCENTRATED SOLUTION.

BY F. FOXTON AND W. J. SHUTT.

*Received 11th March, 1927.*

### Introduction.

The electrochemistry of fused salts is essentially simpler than that of aqueous electrolytes in that one component (water) is eliminated from the system. Thus it might be expected that the properties of molten electrolytes would ultimately prove simpler than those of the corresponding aqueous solutions. On examination, however, the behaviour of fused salts presents the anomaly of indicating a high degree of molecular association.

while at the same time all the phenomena usually coupled with high or complete electrolytic dissociation are observed.

In a review of the accumulated data regarding the constitution of fused salts, R. Lorenz<sup>1</sup> showed that the application of the Eotvos equation to the surface tension of many fused salts indicated an association to the extent of at least four molecules to each aggregate. This conclusion was further borne out by the work of Walden<sup>2</sup> on the latent heats of fusion and vaporisation of such melts.

A similar anomaly has been observed by McBain<sup>3</sup> and co-workers in the case of concentrated solutions of soaps. Their results have indicated the presence of highly charged aggregates ("ionic micelle") consisting of large complexes of fatty ions appreciably hydrated. The high electrostatic charge of the micelle ensures it a high mobility despite its relatively large dimensions.

It seemed that it would be of interest to examine the properties of that type of electrolyte which lies between the conditions of aqueous solutions and those of fused salts. This paper is a description of the investigation of the electromotive forces of cells containing an electrolyte in aqueous solutions so strong as to approach the conditions of molten salts. The electrolyte chosen was zinc chloride. This salt has, at ordinary temperatures, a high solubility which increases continuously as the temperature rises; it also furnishes ions which are reversible with respect to massive electrodes both in aqueous solution and in the fused state.

### Experimental.

*Apparatus.*—The preparation of a reliable zinc electrode presented less difficulty than had been expected from the literature. Pure zinc was cast in hot graphite moulds to the form of small cylinders, which were turned on the lathe to give a bright smooth surface. Success depended on the preservation of this surface from any trace of grease and this was attained by immediate immersion of the freshly turned rods in pure benzene. Shortly before use the electrodes were washed with alcohol and water and plated in an ammoniacal solution of zinc sulphate, as recommended by Richards<sup>4</sup> and Lewis. The electrodes prepared in this way were placed in half element vessels designed to ensure that the zinc was entirely below the surface of the liquid in the thermostat.

Platinum and carbon presented themselves as suitable media for the chlorine electrode. As it was feared that the former might cease to remain passive at the high temperatures to be employed, it seemed desirable to devote considerable attention to the behaviour of carbon, especially as the latter had been previously studied at high temperatures, notably by Lorenz<sup>5</sup> and Fox, who had shown that the carbon-chlorine electrode is reversible and gives readily reproducible potentials in molten chlorides of heavy metals. The results were disappointing however. At ordinary temperatures, even with electrodes of the smallest possible dimensions, the time required for attainment of equilibrium was inordinately long, and up to 60° C. it was impossible to reproduce the potential of such an electrode

<sup>1</sup> "Raumerfüllung u. Ionenbeweglichkeit," p. 265, *et seq.*

<sup>2</sup> P. Walden, *Z. physik. Chem.*, 1909, **65**, 257.

<sup>3</sup> Randall, McBain and White, *J. Amer. Chem. Soc.*, 1926, **48**, 2517. McBain and Bowden, *J. Chem. Soc.*, 1923, **123**, 2417.

<sup>4</sup> Richards and Lewis, *Proc. Amer. Acad.*, 1898, **34**, 87.

<sup>5</sup> Lorenz and Fox, *Z. physik. Chem.*, 1908, **63**, 109.

with greater precision than about 10 millivolts. The results seemed to indicate that, at temperatures higher than those employed in this work, carbon might function satisfactorily and replace the platinum electrodes which had perforce to be used for this research. The metal was platinised

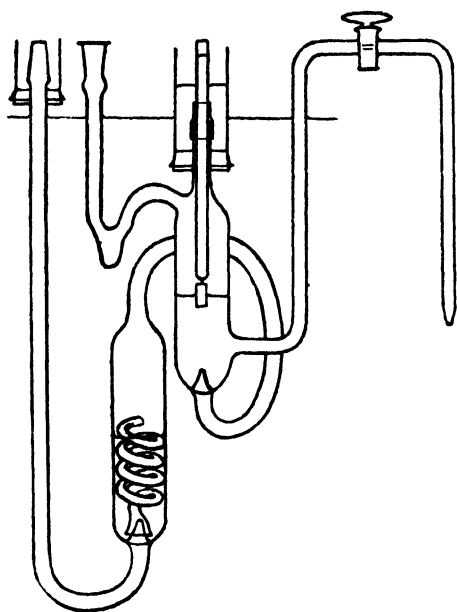


FIG. 1.

for use in solutions below about molal strength, but with higher concentrations bright platinum proved quite satisfactory. The chlorine, prepared by the action of pure hydrochloric acid on cold solid potassium permanganate, was stored over sulphuric acid, and tests by absorption in alkali indicated a purity of over 99.7 per cent. for the gas. The form of electrode vessel and wash bottle adopted for solutions up to 15 molal zinc chloride is shown in Fig. 1. For solutions approaching saturation it was necessary to modify the type of cell to permit of total immersion in the thermostat of the connecting tubes containing electrolyte. Since the vapour pressure of such solutions was comparatively low, previous

washing of the gas was unnecessary and the wash bottle could be eliminated. The form of chlorine and zinc electrode vessels employed for these solutions is shown in Fig. 2. Ground joints and taps were lubricated with the minimum quantity of vaseline and the chlorine came in contact only with sulphuric acid and glass from the moment of its formation until it reached the electrode.

The electrolyte was prepared by dissolving Merck's pure zinc chloride in distilled water. For concentrations below about 7 molal a clear solution was not obtained and recourse had to be had to filtration. Also for saturated solutions, which were made at the temperature of the thermostat, the liquid was drawn through a Jena glass immersion filter. Thus it was impossible

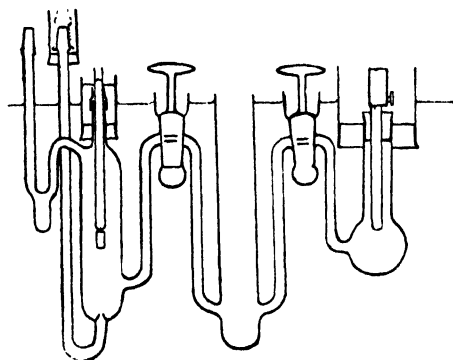


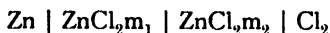
FIG. 2.

to make a solution of predetermined strength. This difficulty necessitated a somewhat laborious analysis of the contents of the cells at the conclusion of an experiment and, furthermore, it considerably complicated the interpretation of the results.

The thermostat was of the usual electrically controlled type and could

be relied on to maintain its temperature within  $\pm 0.02^\circ \text{C}$ . The thermometers, potentiometer, and Weston cell used for the measurements were each standardised against instruments certified by the National Physical Laboratory.

Owing to the high voltages for cells of the type



it was necessary to oppose the constant voltage of a Weston cell to bring the figures within the range of the potentiometer.

*Analytical Method.*—At the end of each experiment samples for analysis were removed from the electrode vessels. Solutions from the gas electrode vessels were analysed for chloride after the chlorine had escaped. A measured quantity of decinormal silver nitrate solution, slightly in excess of the required amount, was added to weighed quantities of the solution in the presence of nitric acid. The excess silver nitrate was estimated by Volhard's "method of titrating with decinormal potassium thiocyanate, using ferric alum as indicator. Results were reproducible to within 0.2 per cent. The zinc content of the solution from around the zinc electrode was estimated by the phosphate method of Tamm<sup>7</sup> as modified by Dakin.<sup>8</sup> The precipitate was weighed as zinc ammonium phosphate. Results were reproducible within 0.15 per cent. Analyses were performed in duplicate. Except in the case of dilute solutions the zinc content was always in excess of the corresponding chloride concentration in the solution. The amount in excess agreed closely with the solubility of zinc oxide in zinc chloride solutions as determined by Driot.<sup>9</sup> It could not be ascribed to solution of the zinc electrode since the same discrepancy between the concentrations was observed in the analysis of zinc chloride solutions used for vapour pressure determinations, where the solutions had been in contact with neither zinc metal nor with chlorine gas.

### Vapour Pressure Measurements.

The interpretation of the results obtained by the use of a chlorine gas electrode involves a correction for the partial pressure of the gas and, since data for the vapour pressures of zinc chloride solutions under the conditions employed were lacking, it became necessary to measure these values to an accuracy of about  $\pm 3$  mm. of mercury. It is thought that the figures presented below are of an accuracy well within these limits.

For vapour pressures at  $60.48^\circ \text{C}$ . a modified form of isoteniscope<sup>10</sup> was used. At this temperature little difficulty was experienced in establishing equilibrium between the solution in the bulb and manometer of the isoteniscope. Dilution of the solution by condensation of water during cooling was avoided by sealing the isoteniscope from the vacuum reservoir and gauge at a point immediately above the surface of the thermostat. The bulb was broken from the isoteniscope and its contents analysed after cooling.

At  $80.4^\circ \text{C}$ . the isoteniscope proved unreliable and a comparison method was adopted. Two solutions, one of zinc chloride and the other of sulphuric acid, were placed in bulbs connected by wide tubing. After evacuation the system was sealed and placed in the thermostat, where it was gently shaken for at least two hours. The breaking of a fine capillary

<sup>6</sup> Volhard, *Ann. Chem. u. Pharm.*, **190**, 23.

<sup>7</sup> Tamm, *Chem. News*, **24**, 148.

<sup>8</sup> Dakin, *Chem. News*, 1900, **82**, 101.

<sup>9</sup> Driot, *Compt. Rend.*, **150**, 1426.

<sup>10</sup> Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412.

tube permitted air to enter the apparatus and practically stopped further distillation during cooling. The contents of both bulbs were analysed. Qualitative tests showed that no mixing had occurred. Sulphuric acid solutions were chosen as reference substances since their vapour pressures have been thoroughly worked out by Burt<sup>11</sup> for a wide range of concentrations and temperatures. Points on the curve were checked at comparatively low concentrations by the replacement of sulphuric acid by saturated solutions of sodium carbonate and sodium sulphate respectively, whose vapour pressures have been determined by Gerasimow<sup>12</sup> and P. Pawlowitsch.<sup>13</sup>

The results of vapour pressure measurements for 60.48° C. and 80.40° C. are given in Table I. In most cases analysis was made for chloride content alone and the values obtained are given in terms of weight of chlorine (as chloride) per 100 grams of solution. In one or two cases the figures were checked by a gravimetric determination of zinc, when for reasons given above, a slight excess of metal was indicated.

TABLE I.

<i>t</i> = 60.48° C.		<i>t</i> = 80.40° C.	
Chloride Per Cent.	Pressure in mm. Mercury.	Chloride Per Cent.	Pressure in mm. Mercury.
0.0	152	0.0	369
3.186	149	12.50	322
6.424	147	16.45	297
9.872	144	16.66	295
11.21	141	16.72	299
12.69	139	21.37	260
15.68	134	23.40	244
19.45	124	28.96	180
20.34	120	37.09	72
21.47	115	38.46	45
26.22	90	—	—
40.16	<7	—	—

### Results and Discussion.

*Cells without Liquid Junction.*—Measurements were made of the electromotive forces of cells of the type  $\text{Zn} \mid \text{ZnCl}_2 \mid \text{Cl}_2 \cdot \text{Pt}$  for both 60.48° C. and 80.40° C., and the results are given in Table II.

The first column of the table indicates the molality (moles of salt per 1000 grams water) of the solution as determined by analysis of zinc content and column two the corresponding figures obtained by chloride determination. The observed voltages for the cells are given in the third column. The last column gives the electromotive forces corrected to a partial pressure of 760 mm. of chlorine.

The corrected voltages were plotted against molalities and from the curves the temperature coefficient for the cell  $\text{Zn} \mid \text{ZnCl}_2(5m) \mid \text{Cl}_2 \cdot \text{Pt}$  was evaluated. It was found to be 0.0007128 volt per degree for the temperature range 60° C. to 80° C. The Gibbs-Helmholtz equation may be applied and leads to the result 105,400 calories as the heat of formation of zinc chloride in 5 molal solution from solid zinc and chlorine gas at a tem-

<sup>11</sup> Burt, *J. Chem. Soc.*, 1904, 85, 1339.

<sup>12</sup> Gerasimow, *Journ. russ.*, 1913, 45, 1666.

<sup>13</sup> Pawlowitsch, *Z. physik. Chem.*, 1913, 84, 170.

TABLE II.

<i>t.</i>	<i>m</i> Zn.	<i>m</i> Cl/2.	<i>E.M.F.</i> (obs.).	<i>E.M.F.</i> (Corr.).
60.48° C.	0.07395	0.07395	2.1740	2.1771
	0.07925	0.07925	2.1703	2.1736
	0.1768	0.1766	2.1561	2.1600
	0.3522	0.3545	2.1385	2.1416
	0.7993	0.7960	2.1137	2.1169
	0.8675	0.8180	2.1148	2.1183
	0.9262	0.8255	2.1130	2.1163
	0.9350	0.9300	2.1135	2.1168
	2.370	2.372	2.0863	2.0892
	2.456	2.399	2.0861	2.0892
	2.572	2.531	2.0804	2.0834
	4.239	4.144	2.0615	2.0640
	4.251	4.152	2.0623	2.0649
	4.547	4.407	2.0546	2.0571
	4.622	4.574	2.0536	2.0561
	4.836	4.719	2.0521	2.0550
	4.939	4.793	2.0506	2.0532
	4.942	4.811	2.0496	2.0522
	12.40	12.01	1.9689	1.9699
	20.47	20.28	1.9183	1.9183
	23.87	23.63	1.9082	1.9086
	24.67	24.49	1.9055	1.9055
	24.99	24.67	1.9047	1.9049
80.40° C.	0.1866	0.1866	2.1299	2.1408
	0.4108	0.4083	2.1004	2.1111
	2.518	2.488	2.0639	2.0725
	2.528	2.490	2.0635	2.0716
	2.596	2.545	2.0631	2.0713
	4.203	4.110	2.0414	2.0488
	4.310	4.180	2.0413	2.0486
	4.942	4.746	2.0335	2.0403
	6.905	6.685	2.0100	2.0161
	20.30	19.77	1.9094	1.9108
	21.16	20.84	1.9034	1.9047
	22.33	21.83	1.9001	1.9014
	25.07	24.43	1.8891	1.8900
	28.72	27.98	1.8816	1.8820

perature of 70° C. Applying Kirchhoff's equation and assuming the value 0.6 calories per gram for the specific heat of 5 molal zinc chloride solution, the heat of reaction at 20° C. is found to be 104,800 calories. The heat of solution when one mole of zinc chloride dissolves to give a 5 molal solution is 7500<sup>14</sup> calories.<sup>15</sup> Subtracting the latter figure the value 97,300 calories is obtained for the heat of formation of zinc chloride at 20° C. The figures obtained by Thomsen<sup>14</sup> and Berthelot<sup>16</sup> are respectively 97,210 and 97,400 calories. Data are not available for heats of solution, etc., for higher concentrations, but an approximate calculation made on the results in 25 molal solution gives a value of about 96,000 calories for the heat of formation of zinc chloride.

The experimental technique adopted in this work is unsuited to the examination of very dilute solutions, and extrapolation to zero concentration for the purpose of determining  $E_0$  is out of the question. However, in order to obtain some idea of relative magnitudes of activity coefficients for various concentrations of the salt, the assumption was made that the zinc

<sup>14</sup> Thomsen, *J. prakt. Chem.*, 1875, II, 410.

<sup>15</sup> Thomsen, "Thermochemistry," ch. III, p. 87.

<sup>16</sup> Berthelot, *Ann. Chim. Phys.*, 1875, 4, 189.

chloride at molal concentration had the same activity coefficient as 1.0 molal barium chloride. The latter has been determined at 25° C. as 0.394.<sup>17</sup> As the activity coefficient changes little with temperature<sup>18</sup> it was felt that the assumption might be carried a little further to cover the difference in temperature. The values given in Table III. have been calculated for round concentrations by means of the relation.

$$E = \frac{3RT}{2F} \ln \frac{\gamma_1 m_1}{\gamma_2 1.0}$$

where  $\gamma_2$  is the activity coefficient of molal barium chloride and  $\gamma_1$  the unknown coefficient of  $m_1$  zinc chloride solution.

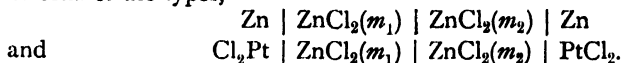
TABLE III.

$t = 60.48^\circ \text{C.}$		$t = 80.40^\circ \text{C.}$	
$m_1$	$\gamma_1$	$m_1$	$\gamma_1$
0.5	0.553	0.5	0.610
(1.0	0.394)	(1.0	0.394)
2.0	0.301	2.0	0.285
3.0	0.285	3.0	0.263
4.0	0.298	4.0	0.269
5.0	0.332	5.0	0.291
6.0	0.379	7.5	0.370
8.0	0.517	10.0	0.480
10.0	0.691	15.0	0.787
12.5	0.961	20.0	1.177
15.0	1.25	25.0	1.50
20.0	1.75	28.0	1.54
25.0	1.97		

These values throughout are less than would be expected on the assumption of similarity between zinc chloride and the alkaline earth chlorides examined by Lucasse.<sup>17</sup> For approximately 3 molal concentration the activity coefficients for strontium and calcium chlorides are respectively 1.05 and 3.5 whereas that found for zinc chloride is only about 0.28 at 60.48° C.

The values for  $\gamma_1$  in Table III. have been plotted against square root of molality and the curves are shown in Fig. 3. The shape of these curves is affected little by assuming other values for  $\gamma_2$ , although the absolute values obtained for activity coefficients of zinc chloride are altered considerably. It is interesting to note the fall off in value of  $\gamma_1$  at the highest concentrations examined.

*Cells with Liquid Junction.*—Measurements were made of the potentials of cells of the types,



The results are given in Table IV. for the temperatures 60.48° C. and 80.40° C. respectively.

The zinc concentration cells behave much in the manner which might be expected, and the results could be combined with those of the cells without liquid junction for the determination of transport numbers by the graphical method employed by Lucasse.<sup>17</sup> The abnormal figures given by

<sup>17</sup> Lucasse *J. Amer. Chem. Soc.*, 1925, 47, 743.

<sup>18</sup> Randall, McBain, and White, *J. Amer. Chem. Soc.*, 1926, 48, 2517.

TABLE IV.

Zn   ZnCl <sub>2</sub> (m <sub>1</sub> )   ZnCl <sub>2</sub> (m <sub>2</sub> )   Zn.				Pt . Cl <sub>2</sub>   ZnCl <sub>2</sub> (m <sub>1</sub> )   ZnCl <sub>2</sub> (m <sub>2</sub> )   Pt . Cl <sub>2</sub> .			
t °C.	m <sub>1</sub> .	m <sub>2</sub> .	E.M.F.	t °C.	m <sub>1</sub> .	m <sub>2</sub> .	E.M.F. (Corr.)
60.48	2.39	0.867	0.0263	60.48	2.38	0.871	+ 0.0019
	2.37	0.882	0.0276		2.40	0.930	+ 0.0009
	4.94	0.079	0.1126		4.79	0.079	+ 0.0077
	4.24	0.177	0.0869		4.14	0.177	+ 0.0093
	4.25	0.356	0.0735		4.15	0.354	+ 0.0030
	4.94	0.926	0.0710		4.65	0.796	- 0.0046
	12.40	4.622	0.1288		4.86	0.818	- 0.0057
	20.47	4.637	0.2042		12.01	4.574	- 0.0426
	23.87	4.814	0.2140		20.28	4.583	- 0.0651
	24.99	4.839	0.2179		23.63	4.705	- 0.0668
					24.67	4.701	- 0.0669
80.40	0.41	0.187	0.0147	80.40	0.41	0.187	+ 0.0145
	4.20	2.518	0.0277		4.11	2.488	- 0.0045
	4.21	2.596	0.0267		4.12	2.538	- 0.0035
	6.90	0.411	0.1175		6.68	0.408	- 0.0117
	20.30	4.310	0.1978		19.77	4.180	- 0.0599
	21.16	4.301	0.2076		20.84	4.168	- 0.0633
	25.07	4.271	0.2225		24.43	4.116	- 0.0653
	28.72	4.942	0.2216		27.98	4.746	- 0.0637

The negative sign indicates that the electrode in the more concentrated solution is positive with respect to that in the dilute.

the chloride concentration cells, however, render the exact nature of the anions a matter of considerable doubt. For all solutions except the most

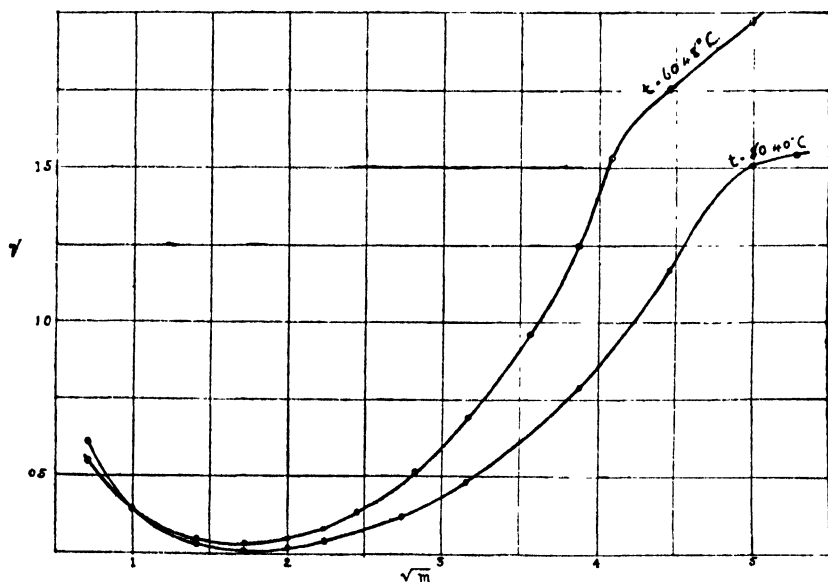


FIG. 3.

dilute, the chlorine electrode in the stronger half of the cell is positive with respect to the electrode in the less concentrated solution. In view of this

result, it is felt that further calculations in this respect may be deferred until more precise information is available.

It is considered unlikely that the abnormal results are in any way due to failure of the chlorine electrode since the value for the heat of formation of zinc chloride obtained from the electromotive force data agrees so well with the accepted calorimetric result. The more probable explanation is that extensive formation of complex anion takes place in concentrated solution. Under such conditions further addition of zinc ion, as zinc chloride, may depress the activity of the chloride ion even below its previous value. The marked fall in the rate of increase of  $\gamma$  with rising concentration (Fig. 3), observed in the strongest solutions examined, may be ascribed to the appearance of some other type of polymerisation under extreme conditions of concentration. This explanation would account for the phenomena observed, but other complications may be present and it is hoped that further work with a somewhat modified experimental method will yield more definite results.

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## THE INFLUENCE OF ELECTROLYTES ON THE SOLUBILITY OF OTHER ELECTROLYTES IN NON-AQUEOUS SOLVENTS.

BY CHARLES A. KRAUS AND RALPH P. SEWARD.

*Received 16th April, 1927.*

This investigation was undertaken for the purpose of securing data showing how the thermodynamic potential of an electrolyte depends on the total concentration of electrolytes in non-aqueous solutions. The solubility method was adopted, since it affords a reasonably accurate method of studying the phenomena in question at concentrations as low as  $10^{-3}$  normal or lower.

Solubility determinations were carried out in acetone and isopropyl alcohol, both solvents having been carefully purified and thoroughly dried. Final drying was effected by means of pulverised boric oxide. Traces of water increase the solubility of an electrolyte in marked degree, but it was found that the relative effects remain practically uninfluenced on the addition of several per cent of water.

The solubility determinations were carried out at  $25.00 \pm 0.01^\circ$ . Approximately 3 litres of solvent were introduced into a closed glass container with an excess of the saturating salt and a known quantity of a second electrolyte. The solutions were rotated in a thermostat at a temperature of about  $30^\circ$  for some hours after which the temperature was reduced to  $25^\circ$  and the solutions rotated for approximately 24 hours to establish equilibrium. The analytical difficulties were considerable and satisfactory results were obtained only when the saturating salt was a halide and the added salt a nitrate, in which case the concentration of the saturating salt was determined as silver halide by gravimetric methods.

## Experimental Results.

The results obtained are given in the following tables which are self-explanatory. All concentrations are expressed in millimols per litre. For convenience, the square root of the total ion concentration and the logarithm of the ion product ratio are included in these tables.

TABLE I.

SOLUBILITY OF SODIUM CHLORIDE IN ISOPROPYL ALCOHOL AT 25° IN THE PRESENCE OF SODIUM NITRATE.

NaNO <sub>3</sub> . . . . .	0.0000	0.0800	0.1672	0.4013	0.5902	0.5984
NaCl (anal.) . . . . .	.4246	.4159	.4050	.3817	.3625	.3640
( $\Sigma c_i$ ) <sup>1/2</sup> × 10 <sup>3</sup> . . . . .	29.14	31.50	33.84	39.57	43.64	43.87
- 1/2 log P <sub>10</sub> /P <sub>i</sub> . . . . .	0.0000	0.0292	0.0544	0.1098	0.1412	0.1442
NaNO <sub>3</sub> . . . . .	0.8539	1.3097	1.5574	1.9590	2.8240	—
NaCl (anal.) . . . . .	.3480	.3242	.3244	.3074	.2903	—
( $\Sigma c_i$ ) <sup>1/2</sup> × 10 <sup>3</sup> . . . . .	49.16	57.16	61.32	67.31	78.91	—
- 1/2 log P <sub>10</sub> /P <sub>i</sub> . . . . .	0.1827	0.2340	0.2645	0.2936	0.3501	—

TABLE II.

SOLUBILITY OF SODIUM CHLORIDE IN ISOPROPYL ALCOHOL AT 25° IN THE PRESENCE OF AMMONIUM NITRATE.

NH <sub>4</sub> NO <sub>3</sub> . . . . .	0.0000	0.0985	0.1839	0.3537	0.6938	1.4024
NaCl (anal.) . . . . .	.455	.481	.503	.547	.617	.734
( $\Sigma c_i$ ) <sup>1/2</sup> × 10 <sup>3</sup> . . . . .	30.16	34.12	37.06	42.45	51.20	65.35
- 1/2 log P <sub>10</sub> /P <sub>i</sub> . . . . .	0.0000	0.0241	0.0436	0.0800	0.1323	0.2027

TABLE III.

SOLUBILITY OF SODIUM BROMIDE IN ACETONE AT 25° IN THE PRESENCE OF SODIUM NITRATE.

NaNO <sub>3</sub> . . . . .	0.0000	0.1371	0.2286	0.6602
NaBr (anal.) . . . . .	.7677	.7597	.7462	.7629
( $\Sigma c_i$ ) <sup>1/2</sup> × 10 <sup>3</sup> . . . . .	39.07	40.68	41.48	45.68
- 1/2 log P <sub>10</sub> /P <sub>i</sub> . . . . .	0.0000	0.0315	0.0457	0.1102

## Discussion of Results.

In a general way the solubility relationships of electrolytes in non-aqueous solvents resemble those in water, that is, the solubility of a salt is diminished on addition of a second salt with a common ion, while it is increased on the addition of a salt without a common ion. However, the order of magnitude of these effects in isopropyl alcohol and acetone is much lower than it is in water.

It is of interest to examine the results from the point of view of the Debye-Hückel theory of dilute solutions of electrolytes. As A. A. Noyes<sup>1</sup> has shown, the solubility effects in aqueous solutions are in excellent agreement with this theory.

In Figs. 1 and 2 are plotted the logarithms of the activation product ratio (Noyes,  $\Delta c_i$ ) against the square root of the total ion concentration.

<sup>1</sup> *J. Am. Chem. Soc.*, **46**, 1098 (1924).

According to the Debye-Hückel theory the logarithm of the activation product ratio should vary as a linear function of the square root of the total ion concentration, and the constants appearing in this equation may be calculated from the known solubility of the salt in the pure solvent and

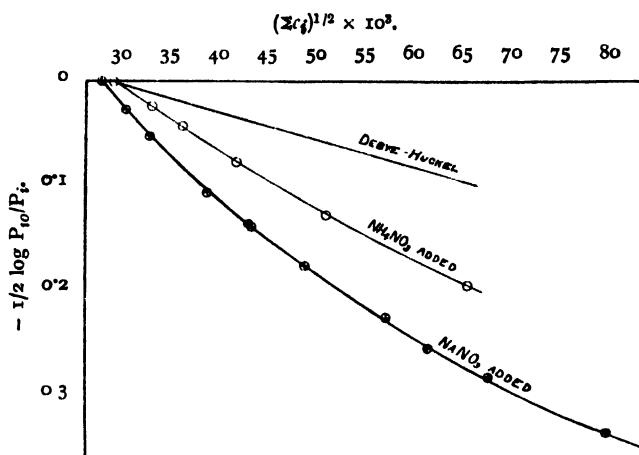


FIG. 1.—Solubility of NaCl in Isopropyl Alcohol in the presence of  $\text{NaNO}_3$  and  $\text{NH}_4\text{NO}_3$ .

the di-electric constant of the solvent. The straight lines drawn in the two figures represent the values predicted according to the Debye-Hückel theory.

As may be seen from the figures, the experimental values diverge largely

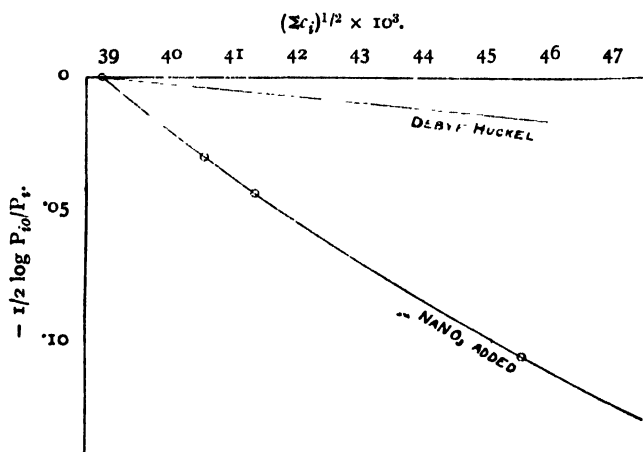


FIG. 2.—Solubility of NaBr in Acetone in the Presence of  $\text{NaNO}_3$ .

from the requirements of the Debye-Hückel theory. It is true that the equations founded on the theory of Debye and Hückel are applicable only at very low concentrations and that we have no means of predetermining how low the concentration must be before deviations may be expected to fall within the limits of experimental error. However, judging by the results obtained in aqueous solutions, it would seem that the necessary conditions

should be at least approximately fulfilled at concentrations in the neighbourhood of  $10^{-3}$  normal. At any rate, it might be expected that the experimental values would approach the predicted curve as a limit. This, however, is not the case. With sodium chloride in the presence of sodium nitrate in isopropyl alcohol, in particular, the curve is strongly convex toward the axis of concentration, and much the same thing is true of sodium bromide in acetone. With sodium chloride in the presence of ammonium nitrate in isopropyl alcohol the curve is more nearly linear. While the thermodynamic potential of the saturating salt is markedly diminished on addition of a second electrolyte, whether with or without a common ion, the magnitude of the effect is much lower than would be predicted on the basis of current theories that ascribe these effects solely to inter-ionic forces.

### Conclusion.

The solubility of a salt in a non-aqueous solvent is depressed on addition of a second salt with a common ion, while it is increased on the addition of a salt without a common ion. The magnitude of these effects in isopropyl alcohol and acetone is much smaller than in water.

The solubility effects in question are not satisfactorily accounted for on the basis of the Debye-Huckel theory. Evidently this theory cannot be applied to solutions in solvents of lower dielectric constant without modification. There are not a few facts that indicate that in solvents of lower dielectric constant it will be necessary to let fall the assumption that the only molecular species present are the simple ions.

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## THE USE OF AMALGAM ELECTRODES FOR DETERMINING ACTIVITIES IN METHYL ALCOHOL.

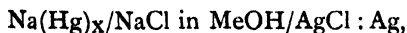
BY J. H. WOLFENDEN, C. P. WRIGHT, N. L. ROSS KANE, AND  
P. S. BUCKLEY.

*(Received 29th March, 1927.)*

Owing to the impracticability of making precise freezing-point determinations in methyl alcohol solutions, measurements of *E.M.F.* assume a peculiar importance as the principal source of information as to the activities of electrolytes in this solvent. The restrictions imposed by the limited number of truly reversible electrodes and by the presence of complex ions even in dilute solutions virtually confine us to measurements of the halides of hydrogen, the alkali metals and the alkaline earth metals. Nonhebel and Hartley<sup>1</sup> have carried out measurements of the *E.M.F.* of the cell,



over a range of molality from  $M/2$  to  $M/2000$  and have used the results to calculate the activity of hydrogen chloride in methyl alcohol. The present note is concerned with an attempt to carry out similar measurements with the cell,



It was hoped that, as in the case of hydrogen chloride, it would be possible to carry out accurate measurements in sufficiently dilute solution to permit of the evaluation of absolute activity coefficients by graphical extrapolation to infinite dilution. Such a method avoids the element of uncertainty introduced by the alternative method of assuming a value of the activity coefficient for a given concentration, based on conductivity data or other considerations. For the purposes of such graphical extra-

polation, measurements may be made with either the single cell indicated or with a combination of two such cells forming a concentration cell without transport, provided, in the latter case, that the concentration pairs are chosen so as to provide a continuous "ladder" from the strong to the dilute solutions.<sup>2</sup> It was thought preferable to avoid the double cells used by previous workers on methyl alcohol,<sup>3</sup> as these might conceal any secondary effects at the pair of intermediate amalgam electrodes.

Measurements were therefore carried out with the cell,  
 $\text{Na(Hg)}^x/\text{NaCl}$  in

$\text{MeOH}/\text{AgCl}:\text{Ag}$ ,

over a range of molality from  $M/10$  to  $M/2000$ . The methyl alcohol was prepared in the manner described by Hartley and Raikes<sup>4</sup> except that the final distillation into the block tin condenser was carried out in a stream of dry nitrogen. The product showed a specific conductivity averaging  $0.003$  gemmhos and a viscosity test indicated a maximum water content of  $0.015$  per cent. Merck's sodium chloride, dried on a quinoline bath, was dissolved

in the methyl alcohol in flasks filled with nitrogen. The silver-silver chloride electrodes were chloridised in an approximately decinormal solution of sodium chloride in methyl alcohol; the two electrodes employed in each measurement agreed with one another to  $0.1$  millivolt. The sodium amalgam was prepared by the electrolysis of saturated aqueous sodium carbonate and was filtered through a very fine capillary into the amalgam reservoir where it was kept under an atmosphere of nitrogen. Its concentration was estimated by treatment with a known excess of standard acid in the manner described by Richards and Conant.<sup>5</sup>

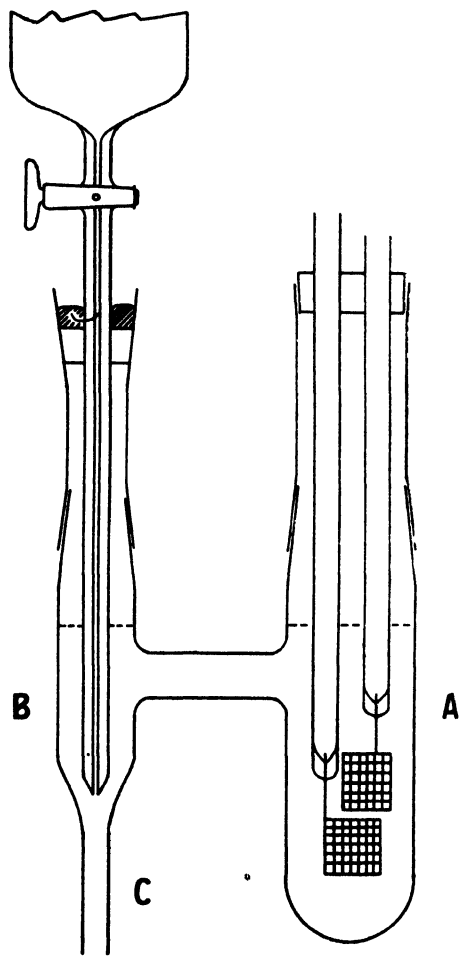


FIG. 1.

After a few preliminary measurements, a cell of the type illustrated in Fig. 1 was employed. The right limb A contains the pair of silver-silver chloride electrodes. The left limb B contains the streaming amalgam electrode. The volume of A was about 40 cubic centimetres while B had a capacity of three or four cubic centimetres to ensure the most rapid rate of renewal of solution round the amalgam tip for a given expenditure of solution. Preliminary experiments had shown that if the left limb had as large a capacity as that on the right, decomposition was so fast as to cause the *E.M.F.* to drop steadily from the first measurement onwards, at a rate dependent on the dilution of the solution. For similar reasons the amalgam tip was ground to a conical form and placed at the point where the solution stream would be approaching its maximum velocity. With the modified form of cell illustrated there was no falling off of *E.M.F.* with time nor did the *E.M.F.* vary appreciably with the rate of solution flow. The cell was filled with nitrogen before the solution was admitted. The solution entered B from behind at a point just above the amalgam tip, after passing through a long zig-zag of thin-walled tubing to ensure temperature equilibrium. Both solution and amalgam left the cell at C. The rate of solution flow was about 8 to 10 cubic centimetres per minute; the rate of amalgam flow was varied from 1 to 30 drops per second corresponding to expenditures of  $\frac{1}{2}$  to 10 cubic centimetres of amalgam per minute. A wide range of amalgam concentrations (from 0.4 per cent. to 0.001 per cent.) was tried; the most satisfactory concentration from the point of view of steadiness of *E.M.F.* was in the neighbourhood of 0.04 per cent. There was some indication of the advantages of "matching" the amalgam concentration to the concentration of the solution being measured, as recorded by Knobel.<sup>6</sup> On the other hand amalgams as dilute as 0.00135 per cent. and 0.00294 per cent., similar to those used by recent workers, invariably failed to give a steady *E.M.F.*

The most interesting point on the experimental side which emerged from the measurements was the dependence of the *E.M.F.* of the cell upon the rate of flow of the amalgam. From the outset of the experiments it became clear that the potentiometer null-point could be shifted by comparatively small changes in the rate of flow. The point was investigated in some detail by carrying out runs in which the rate of flow was changed many times and the corresponding *E.M.F.* was measured at frequent intervals. In these runs two amalgams of concentrations 0.041 per cent. and 0.00294 per cent. were used and three solutions, M/20, M/200 and M/2000 respectively. Three standard rates of flow were employed, namely 2 drops per second, 8 drops per second and a rate described as "semi-continuous" in which individual drops could scarcely be discerned. With the more dilute amalgam, *E.M.F.* readings were most irregular and it seemed almost impossible to predict even the sense in which a change in the rate of flow would affect the *E.M.F.* At different times in the same run a change from 8 drops per second to "semi-continuous" might cause the *E.M.F.* to rise 3 millivolts or to drop 6 millivolts. A lowering of *E.M.F.* with increase in the rate of amalgam flow seemed to be more frequent than the opposite effect. With the stronger amalgam the results were much more consistent and of an interesting nature. As an example the experiment with 0.41 per cent. amalgam in a solution 0.0568 molar is represented in Fig. 2. The abscissæ give the time in minutes from the beginning of the run, the ordinates represent potentiometer readings in ohms, one ohm corresponding to 0.3 mv.

The results suggest that the cell has a characteristic *E.M.F.* for every

rate of amalgam flow, and no evidence is afforded that there is any limiting rate above which further increases in the rate of flow have no effect on the *E.M.F.* It was further observed that, on changing the rate of flow, equilibrium was not established instantaneously but that the *E.M.F.* drifted during a period of one-half to two minutes towards the value characteristic of the new rate of flow.

The cause of these phenomena is obscure. Other workers have recorded no observations of a similar nature. This may perhaps be connected with the fact that the majority of measurements have been made with double cells in which effects of the nature described would tend to neutralise each other. It is difficult to believe that decomposition at the amalgam surface is entirely responsible for the effect and that the increase of *E.M.F.* with rate of flow is simply due to diminished decomposition. If this were so, one would expect the effect of changing the speed from 2 to 8 drops per

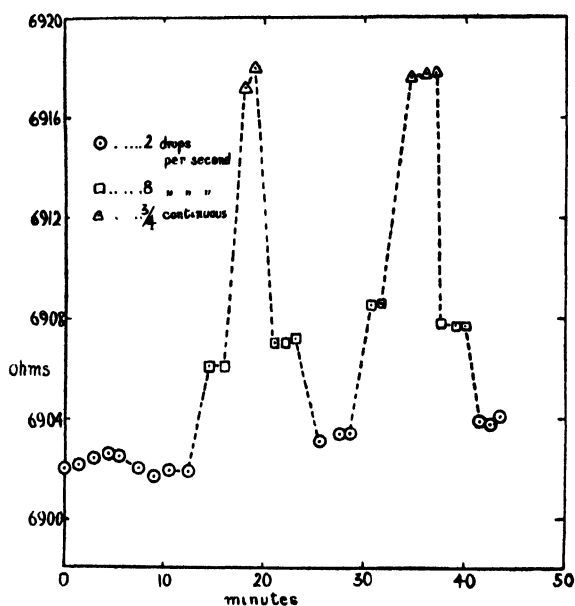


FIG. 2.

second to be as great as, or even greater than, that of a further increase to the "semi-continuous" rate of about 30 drops per second. One would also expect the effect to be most marked in the most dilute solutions and almost absent from a solution as concentrated as  $M/20$ , whereas it is roughly the same at all concentrations from  $M/20$  to  $M/2000$ . It seems more likely that electrocapillary and electrokinetic effects are partially or wholly responsible for this

phenomenon which, whatever its causes, destroys all assurance that we are measuring the true equilibrium which we are seeking.

Another equally unexpected effect was brought to light when a series of *E.M.F.*'s, measured at a fairly uniform rate of amalgam flow in a range of solution concentration from  $M/6$  to  $M/2000$ , were plotted so as to arrive at a value for  $E_0$ , the *E.M.F.* of the cell with a solution of unit activity. From the values of Richards and Conant<sup>5</sup> all *E.M.F.*'s were reduced so as to refer to the sodium metal electrode. From these reduced *E.M.F.*'s the four functions  $E_0'$ ,  $E_{0A}$ ,  $E_0$  (Debye), and  $E_0$  (Milner) were calculated, as described by Hartley and Nonhebel<sup>1</sup> from the equations:

$$(1) E_0' = E + 0.11831 \log c.$$

$$(2) E_{0A} = E + 0.11831 \log c + 0.11831 \log \frac{\Lambda c}{\Lambda_0}.$$

$$(3) E_0 \text{ (Debye)} = E + 0.11831 \log c + 0.11831 \log f \text{ (Debye).}$$

$$(4) E_0 \text{ (Milner)} = E + 0.11831 \log c + 0.11831 \log f \text{ (Milner).}$$

The volume concentrations  $c$  were obtained by multiplying the concentrations per thousand grammes of solution by 0.7864, the density of pure methyl alcohol. The results are given in the following table:

M.	$\sqrt{c}$	E.	$E_0'$	$E_{0\Lambda}$	$E_0$ (Debye).	$E_0$ (Milner).
0.00067	0.0229	3.0476	2.6591	2.6565	2.6534	2.6551
0.00085	0.0258	3.0324	2.6568	2.6513	2.6504	2.6523
0.00166	0.0362	3.0280	2.6870	2.6825	2.6780	2.6807
0.00395	0.0558	3.0032	2.7066	2.6993	2.6927	2.6970
0.00726	0.0759	2.9816	2.7167	2.7063	2.6978	2.7039
0.00817	0.0801	2.9772	2.7178	2.7075	2.6978	2.7042
0.01654	0.1140	2.9483	2.7252	2.7110	2.6967	2.7062
0.01654	0.1140	2.9497	2.7266	2.7124	2.6981	2.7076
0.0361	0.1683	2.9129	2.7298	2.7106	2.6877	2.7025
0.0558	0.2109	2.9023	2.7424	2.7194	2.6897	2.7088
0.0748	0.2420	2.8886	2.7428	2.7175	2.6833	2.7046
0.1581	0.3510	2.8586	2.7510	2.7184	2.6633	—

The four functions should converge to a common limiting value at infinite dilution, equal to  $E_0$  the *E.M.F.* of the cell with a sodium chloride solution of unit activity. When plotted against the square root of the concentration we should expect that, as in the case of hydrogen chloride in methyl alcohol, the curves of the four functions should approach linearity below  $\sqrt{c} = 0.10$  and should approach the axis of zero concentration at a finite angle.

In Fig. 3,  $E_0'$  and  $E_0$  (Debye) are plotted against the square root of the concentration; these two functions only are plotted for the sake of clear-

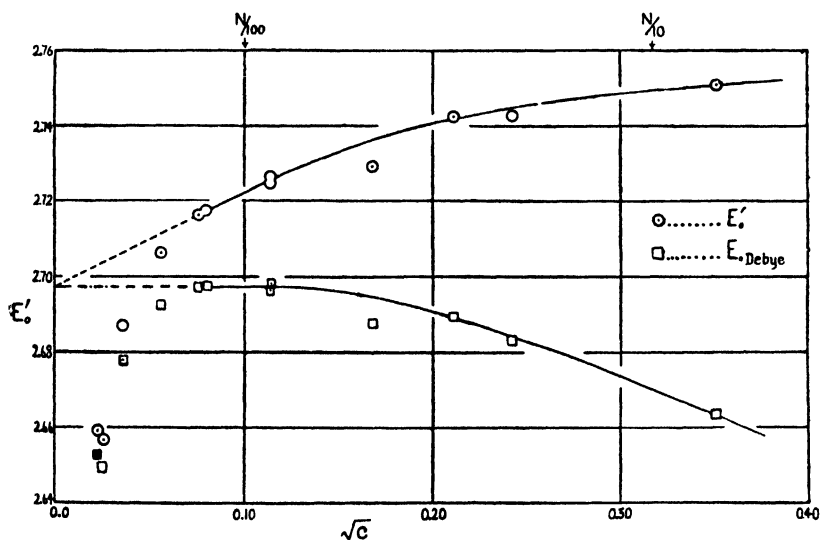


FIG. 3.

ness. Contrary to expectation both functions are seen to fall rapidly below  $\sqrt{c} = 0.07$  and to approach the vertical axis asymptotically instead of merging into straight lines which, in the case of the Debye function, would be horizontal if the hypothesis is an accurate representation of the facts. The difference between the anticipated and the observed results corresponds

to differences of 20 to 45 millivolts in the *E.M.F.*'s measured. It is difficult to connect this with the variation of *E.M.F.* with rate of flow, because the extent of that effect seemed to be roughly independent of the concentration; it is unlikely that it is due to decomposition of the amalgam because three of the points plotted (which are in agreement with the rest of the values) are the result of measurements made with the highest rate of amalgam flow. The cause of the phenomenon is at present obscure but, in view of the general agreement between experimental activity values and the Debye theory, the rapid fall of values of  $E_0'$  in very dilute solutions must be assumed not to correspond to true equilibria. There is distinct evidence that the effect has been encountered by other workers using amalgam electrodes.

In the presence of a disturbing influence of such magnitude it is difficult to arrive at any value for  $E_0$  from which activities might be calculated. The best that we can do is to assume that the limiting slope of  $E_0'$  and similar curves is represented by the points between  $\sqrt{c} = 0.12$  (above which concentration all *E.M.F.* measurements indicate appreciable curvature in  $E_0'$ ) and  $\sqrt{c} = 0.07$  (below which it is clear from Fig. 3 that the secondary effect at high dilutions is becoming pronounced). This throws the whole responsibility on four *E.M.F.* determinations; drawing a straight line through the corresponding values for  $E_0'$  and  $E_0$  (Debye), we get lines cutting the axis of zero concentration at  $E_0 = 2.697$  volts. Such an extrapolation assumes that all the *E.M.F.*'s below  $\sqrt{c} = 0.07$  are subject to an unknown experimental error and that the true *E.M.F.*'s over this concentration range are such as would give  $E_0'$  values lying on the rectilinear extrapolation.

A table of activities at round concentrations calculated on this basis is given below. The third column gives the activity coefficient calculated from the smoothed  $E_0'$  curve of Fig. 3; the fourth column gives the corresponding activity coefficient for hydrogen chloride in methyl alcohol; the fifth column gives the value corresponding to the limiting Debye equation,

$$-\log_{10} f = A\sqrt{c},$$

while the sixth column was obtained by adjusting a suitable value of  $a$  in the equation,

$$-\log_{10} f = \frac{Ac}{1 + a\sqrt{c}}$$

For methyl alcohol  $A = 2.112$  and  $a$  was made equal to 1.00.

$c$ .	$\sqrt{c}$ .	$f$ .	$f(\text{HCl})$ .	$f(\text{Debye} - 1)$ .	$f(\text{Debye} - 2)$ .
0.0001	0.0100	0.943	0.966	0.953	0.953
0.0005	0.0223	0.890	0.927	0.897	0.899
0.001	0.0316	0.856	0.900	0.858	0.862
0.005	0.0707	0.705	0.785	0.709	0.725
0.01	0.1000	0.615	0.707	0.615	0.643
0.05	0.2236	0.408	0.516	0.337	0.411
0.10	0.3162	0.367	0.442	0.215	0.311

As in the case of hydrogen chloride, the  $\log f/\sqrt{c}$  curve turns off too sharply in the more concentrated solutions to be represented by the above equations. Up to a concentration of  $c = 0.01$ , however, the activity coefficients correspond closely to the limiting equation of Debye. Too much importance

must not be attached to this result owing to the uncertainty attaching to the extrapolation to  $E_0$  and to the sensitiveness of the  $\log f$  slope to small changes in  $E_0$ . The latter is such that the difference between the limiting slopes of Milner and of Debye corresponds to a difference of no more than eight millivolts in  $E_0$ . The agreement with the Debye slope does however tend to confirm the view that some secondary effect intervenes at about  $\sqrt{c} = 0.07$  and to support the rather arbitrary method of extrapolation which ignores the experimental values below this latter concentration.

Reviewing the results of these preliminary measurements with an amalgam cell in methyl alcohol, it may be said that two unexpected phenomena were disclosed, both of which placed unsuspected obstacles in the way of accurate activity determinations by the *E.M.F.* method. It was found that the *E.M.F.* depended on the rate of flow apparently without limit and irrespective of the concentration of the solution. It was further found that, at concentrations of about  $M/200$  and below, an unknown factor intervened to make the *E.M.F.* twenty to forty millivolts lower than those corresponding to ionic activities of the solutions calculated from Debye and Hückel's equation.

The first of these phenomena needs further detailed investigation before we can feel any certainty as to the significance of an *E.M.F.* measured under these conditions. The influence of the bore of the capillary dropper must be examined as well as that of the concentration of the amalgam and the solution. Comparisons with an electrode of the overflowing cup type would probably be illuminating. The second phenomenon, corresponding to even greater aberrations in the *E.M.F.*'s measured, is particularly important in view of the limitations it places upon the determination of activities by extrapolation to infinite dilution.

#### Note on the Transport Number of the Sodium Ion.

Measurements were made for three pairs of solutions with the liquid-junction concentration cell,

Ag : AgCl/NaCl, conc.  $c_1$ /NaCl conc.  $c_2$ /AgCl : Ag.

The absence of the amalgam electrode made it possible to obtain values concordant to 0.03 mv. The fourth column in the following table gives the value of the *E.M.F.* measured in this way; the fifth column gives the *E.M.F.* of the corresponding concentration cells without liquid junction. The latter were calculated from the *E.M.F.*'s of the single amalgam cell by interpolation on a smoothed curve of  $(E + 0.11831 \log M)$ . The last column gives the values of  $\eta_{Na}$ , the transport number of the sodium ion.

$M_1$ .	$M_2$ .	$\sqrt{M_1 M_2}$ .	E (Liquid Junction).	E (no Liquid Junction).	$\eta_{Na}$ .
0.1790	0.0180	0.0568	0.04415	0.0937	0.471
0.0991	0.00999	0.03146	0.04414	0.0902	0.489
0.0180	0.00204	0.00606	0.04514	0.0901	0.501

The drift of the transport number with concentration may be wholly or partially due to the secondary effect which depresses the *E.M.F.* of the amalgam cell at high dilutions.

Although the values of  $(E + 0.11831 \log M)$  were smoothed like the curve of  $E_0'$  in Fig. 3 to neutralise this disturbing effect, it is probable that the depression of *E.M.F.* is not entirely effaced by the smoothed values

used for the more dilute solutions. However that may be, the values for the transport number give additional confirmation that the *E.M.F.*'s of the amalgam cell below  $\sqrt{c} = 0.07$  cannot represent true equilibrium, for if the experimental *E.M.F.*'s are used over this concentration range, the transport number varies rapidly in dilute solution yielding values which are incompatible with the known mobilities of the two ions.

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- <sup>2</sup> Hückel, *Physik. Z.*, **26**, 126, 1925.
- <sup>3</sup> Pearce and Mortimer, *J. Am. Chem. Soc.*, **40**, 522, 1918.
- Pearce and Hart, *J. Am. Chem. Soc.*, **44**, 24, 1922.
- <sup>4</sup> Hartley and Raikes, *J. Chem. Soc.*, **127**, p. 524 (1925).
- <sup>5</sup> Richards and Conant, *J. Am. Chem. Soc.*, **44**, p. 601 (1922).
- <sup>6</sup> Knobel, *J. Am. Chem. Soc.*, **45**, 70, 1923.

## THE SIGNIFICANCE OF THE ACTIVITY COEFFICIENT.

BY MERLE RANDALL.

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In the development of the theory of solutions, there have been formulated, not only the purely thermodynamic treatments, but also various mechanisms to aid us in explaining the behaviour of these interesting systems. As the formulæ derived thermodynamically often resemble, and are, therefore, often confused with, those derived from a mechanistic viewpoint, it is well to consider the limitations of the thermodynamic method.

The science of thermodynamics cannot take cognisance of the molecular mechanism of a process or of the nature and character of the various molecular species concerned. A pure substance obeys the same rigorous thermodynamic laws whether its molecules are all of one sort, as we imagine them to be in hexane or fluorobenzene, or diversified as we assume them to be in water. The only thermodynamic requirement is that the various molecular species be in extremely rapid equilibrium.<sup>1</sup>

Bancroft<sup>2</sup> has criticised the thermodynamic or activity concept because "... the activities are the values which one must substitute for the concentration in order to make the formulæ fit." This, he continues, means "that we give up all attempts either to test or improve our formulæ." Bancroft has given a clear and correct definition of the activity as used in the purely thermodynamic formulæ, derived rigorously from the second law of thermodynamics. These formulæ are, therefore, true if we are willing to accept the validity of the second law.

Some extremists have refused to recognise the existence of atoms, molecules or electrons. In fact, if the composition of a solution is expressed by the percentages of the various substances present, the thermodynamics of the

<sup>1</sup> See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 11 and 85.

<sup>2</sup> Bancroft, *J. physical Chem.*, **30**, 1194 (1926).

system can be readily formulated. In the case of concentrated aqueous solutions of sulphur trioxide or of phosphorus pentoxide the results obtained may be as simple as when the composition of the solution is expressed in terms of mol fractions of chosen molecular species. However, the use of mol fraction as a unit of composition, need not imply the actual existence of molecules, for the molal weight or formula weight, thermodynamically, can be looked upon as convenient unit of mass without further implications.

The activity concept is a thermodynamic device which has made it possible to bring into agreement the results of the various experimental methods of measuring the colligative properties of a solution. Having chosen to express the composition of a solution in terms of particular molecular species (without regard to the actual existence of these molecules), the activity coefficient gives us a simple empirical expression for the properties of this solution as compared with a perfect solution of the same composition. The perfect solution is one which obeys the generalised statement of Raoult's Law as defined by Lewis.<sup>3</sup> (The fugacity of each constituent is proportional to the mol fraction of that constituent at every temperature and at every pressure.) Because this law is a limiting law in dilute solution (approached in dilute solutions by the laws derived from the mechanistic hypotheses), agreement with the law of the perfect solution has become a criterion of the correct choice of a molecular mechanism a solution.

When we study a solution we make purely arbitrary choices of the chemical species of which we consider the solution composed. In aqueous solutions the solvent, water, is known to consist of many kinds of molecules. The relative amounts of the different molecular species are known to change with the temperature or when a solute is added, yet in the absence of any method of determining these amounts we arbitrarily choose to consider that the solvent consists of a single species, namely  $H_2O$ . Since the other species are in rapid equilibrium with this species, thermodynamics gives us consistent results, although the change of the activity of the water with temperature or composition may not follow any simple law.

So also we make arbitrary assumptions in the choice of the solute. Consciously or unconsciously we are led to choose the formulæ of the dissolved substances so that Raoult's Law is satisfied. The substances so chosen need not actually be present in appreciable amounts, their choice is extra-thermodynamic and any substances in rapid equilibrium with the constituents would serve just as well.

Bancroft's<sup>2</sup> statement that the proponents of the activity concept are not interested in what happens when a neutral salt is added to an acid solution is hardly true. The change in the activity coefficient of the acid is a numerical statement of the changed conditions. But to invent a mechanism such that all the substances will follow exactly the law preferred by a particular author may involve greater empiricism than is implied in the statement that the activity coefficient has changed by a certain amount. However, if we choose a simple mechanism and the thermodynamic machine finds that the deviations from the law of the perfect solution are small, we consider the problem solved. But, if, on the other hand, the thermodynamic machine finds the deviations large, we may either invent a more complicated mechanism, or accept the activity coefficient as the measure of the insufficiency of the simple mechanism.

<sup>3</sup> Lewis, *J. Amer. Chem. Soc.*, **30**, 668 (1908); Lewis and Randall, *Ref. 1*, p. 222.

For example, the ionic theory offered a mechanism which reduced the enormous deviations from the law of the "perfect solution" when a salt is dissolved in water. The inter-ionic attraction theory of Debye and Hückel<sup>4</sup> still further reduces these deviations by taking into account the effect of the inner-ionic electrical forces in the mechanistic formulæ. Bjerrum<sup>5</sup> has offered still another mechanism to take care of deviations from the simple inter-ionic attraction theory, but always there will remain a small correction number or activity coefficient to suggest further mechanistic inventions.

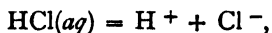
On the other hand no one has been able to invent a molecular mechanism involving the formation of complex substances which will account for the deviations observed when two liquid phases are formed.<sup>6</sup>

*Hydrated Solutes.*—If the solute is known to be hydrated, the anhydrous species is nevertheless usually chosen. Numerous exceptions to this rule are made, however; for example we take  $\text{NH}_4\text{OH}$  rather than  $\text{NH}_3$ ,  $\text{H}_2\text{SO}_4$  rather than  $\text{SO}_3$ , but use  $\text{HCl}$  rather than  $\text{H}_3\text{ClO}$ . If  $x$  molecules of water are assumed to be combined with each solute molecule then in a molal solution of the unhydrated solute we would have 1 mol. of hydrated solute per  $1000 - 18.01x$  grams of water, or the molality on the new basis is greater. Many efforts have been made to explain the deviations of a solution of sugar from Raoult's Law by calculating a composition of the solute which would exactly satisfy the law of the perfect solution, but these calculations usually involve different solvations at different concentrations, and are thus in a sense just as empirical as the activity coefficient itself.

*Strong Electrolytes.*—Since we find experimentally that the activity of a hydrogen chloride solution varies approximately as the square of the molality in the most dilute solutions, we define the standard state or condition of unit activity of the solution in such a way that the activity of the hydrogen ion and of the chloride ion is equal to the molality in an infinitely dilute solution, rather than in such a way that the activity of the hydrogen chloride is equal to its molality, an assumption which could be followed through thermodynamically but with rather complicated expressions.

Many authors have also assumed that the solution consists wholly of ions (complete dissociation), and Debye and Hückel<sup>4</sup> have shown that if the ions are assumed to obey Raoult's Law in a classical sense, then the actually found activity coefficient may be nearly represented by taking into account the inter-ionic electrical forces.

Two important assumptions are tacitly made in the above definition of the standard state. The first is that for a reaction such as



we may write,

$$K = a(\text{H}^+) \times a(\text{Cl}^-)/a(\text{HCl}) = 1; \Delta F^\circ = 0. \quad (1)$$

where  $K$  is the equilibrium constant and  $\Delta F^\circ$  is the increase in free energy when all the substances are in their standard states or at unit activity. In other words a suitable standard state of the undissociated hydrogen chloride is arbitrarily chosen so that the mathematical relationship implied in Equation 1 is always satisfied. It seems hopeless to attempt to define a standard state for the undissociated acid in terms of its molality as such, as can be done in the case of acetic acid and other weak electrolytes, where

<sup>4</sup> Debye and Hückel, *Physikal. Z.*, **24**, 185 (1923).

<sup>5</sup> Bjerrum, *Det. Kgl. Danske Videnskab Selskab Math.-fys. Medd.*, **7**, No. 9 (1926).

<sup>6</sup> See discussion by Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924.

we may from the behaviour in the concentrated solution take the standard state of acetic acid in such a way that the molality of the undissociated acid (corrected for the fraction dissociated) is equal to its molality in dilute solutions.

Randall and Failey<sup>7</sup> have found that the activity coefficient of the undissociated part of a moderately strong acid, such as dichloroacetic acid, as well as that of weak acids, is affected by the presence of ions and, even if we were able to determine the molality of the undissociated hydrogen chloride as such, we should be forced to consider its activity coefficient in the presence of its ions.

The second assumption is that for the hydrated substances we may write:—

$$\begin{aligned} \text{H}^+ + \text{Cl}^- + x\text{H}_2\text{O} &= (\text{H} \cdot y\text{H}_2\text{O})^+ + (\text{Cl} \cdot z\text{H}_2\text{O})^-; \\ K &= [a(\text{H} \cdot y\text{H}_2\text{O}^+) \times a(\text{Cl} \cdot z\text{H}_2\text{O}^-)]/[a(\text{H}^+) \times a(\text{Cl}^-) \times a^x(\text{H}_2\text{O})] = 1; \\ \Delta F^\circ &= 0. \quad (2) \end{aligned}$$

or

$$\text{H}^+ + \text{Cl}^- + x\text{H}_2\text{O} = \text{HCl} \cdot x\text{H}_2\text{O}; \quad K' = a(\text{HCl} \cdot x\text{H}_2\text{O})/[a(\text{H}^+) \times a(\text{Cl}^-) \times a^x(\text{H}_2\text{O})] = 1; \quad \Delta F^\circ = 0. \quad (3)$$

the activity of the hydrogen and chloride ion being defined in the usual manner, and that of the hydrated ions or hydrated undissociated substances being assumed to change in such a manner that  $K'$  always remains equal to unity. In order to use a separate standard state for the hydrated ions and undissociated acid, it would be necessary to know the molality of each of these substances over a range of concentration. It does not seem possible ever to obtain these data experimentally, and the assumption of Equation 1 is therefore justified.

Since the molality of the hydrated or of the unhydrated ion is the same at infinite dilution, the standard state of these substances is the same as that taken for the unsolvated ion. Bjerrum<sup>8</sup> has qualitatively explained the abnormally high activity coefficient of the ions of hydrochloric acid by assuming hydration and taking the molality equal to the mols of acid per 1000 g. of uncombined water.

*Concentration, Molality or Mol Fraction.*—In considering aqueous solutions, it is the usual practice to express the composition as concentration in mols per litre or as molality in mols per 1000 g. of water in vacuum. Since the concentration changes with the temperature owing to the expansion of the solution, the composition in terms of mols per litre is not a desirable thermodynamic function and should not be used. The molality is proportional to the mol fraction in dilute solutions, but the ratio is larger in the more concentrated, and becomes infinity in the limit, or pure solute.

Since all solutions approach the laws of the perfect solution with increasing dilution, it is convenient to define the standard state, or condition of unit activity, of both the solvent and solute with reference to the dilute solution. Hence, we define the activity of a molecular species of a solute as equal to its molality in the infinitely dilute solution. Although the mol fraction is theoretically a more desirable unit of composition, there are many advantages in using molality in the practical calculation of activity coefficients.

Obviously, even if the solution obeys Raoult's Law over the whole range, *i.e.* perfect solution, this definition would require a decrease of the

<sup>8</sup> Bjerrum, *Medd. Vetenskapsakad. Nobelinst.*, 5, No. 16 (1919).

<sup>7</sup> Randall and Failey, unpublished.

activity coefficient by nearly two per cent. in a molal solution, due to the change in the ratio of the molality to the mol fraction. In using the activity coefficient as a criterion of the correctness of a mechanism we must take into account the effect of this change.

*Summary.*—We must recognise that thermodynamics is not concerned with the mechanism of a process. If we express the composition of a solution in terms of the molecular weights of arbitrarily chosen molecular species, then the activity coefficient gives us a simple numerical statement of the deviation of this solution from the law of the perfect solution. The laws based upon various mechanistic hypotheses all tend to approach the law of the perfect solution as a limit. The activity concept has enabled us to bring the various colligative properties of a solution into agreement. It offers, therefore, a test and a guide to the adequacy of the various mechanisms which may from time to time be proposed.

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## METHODS OF CALCULATION OF ACTIVITY COEFFICIENTS.

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A large portion of the data from which activity coefficients can be calculated has been studied in this laboratory. The methods of calculation have been gradually developed and modified in such a way that the experimental results from the various sources can be directly compared. Graphical methods in which small experimental differences, especially in the dilute solutions, are made evident have been found to be the most satisfactory, both from the standpoint of rapidity of treatment and the ease with which a weighted mean of all the data can be obtained.

It is the purpose of this paper to present the methods, some of which have not been previously described, which are most used. No attempt will be made to develop the theory, but for the notation and derivation of the fundamental equations the reader is referred to the work of Lewis and Randall.<sup>1</sup>

Composition is expressed throughout as molality (mols per 1000 g. of water in vacuum). Although it may appear to be an unimportant detail, the error involved in converting the data, when expressed in mols per litre, is often greater than that of the experiments themselves and prevents the full use of otherwise excellent data. The composition of a solution when expressed as mols per litre changes with the temperature owing to the expansion of the solution when heated. In a few cases the transformation to molalities has been found impossible, and we have used a different activity coefficient referred to mols per litre; but as it is almost impossible to determine the temperature coefficient of such a quantity its use is limited to the temperature at which it was determined.

<sup>1</sup> Lewis and Randall, (a) *J. Amer. Chem. Soc.*, **43**, 233, 1113 (1921); (b) "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

The determinations of the activity of the solute may be divided into two classes: first, those which determine the relative activity of the solute and, second, those which determine the activity of the solvent and, by means of the partial molal equations, give the activity of the solute. Simple functions of the experimental results are found and presented in such a form that the results of each class may be compared. Although we shall discuss only the aqueous solution, the procedure may be readily adapted for use with non-aqueous solutions.

### Activity Coefficients of Aqueous Solutions from Determinations of the Activity of the Water.

The following experimental methods all give the activity of the water: freezing-point lowering, vapour pressure lowering, boiling-point raising, osmotic pressure, dew-point lowering, distribution ratio of the solvent and, in the case of a few solvents, measurements of the electromotive force in which the solvent is the substance involved in the electrode reactions.

Two of these methods, the freezing-point lowering and the boiling-point raising, give the activity of the water at the freezing- or boiling-point of the solution rather than at a constant temperature, but fortunately the change of the activity with temperature is small and we have methods of accurately estimating this change.<sup>2</sup>

*Freezing-Point Lowering.*—For the freezing-point lowering, Lewis and Randall used a divergence function,<sup>3</sup>

$$j = 1 - (\theta/\nu\lambda m), \quad . \quad . \quad . \quad (1)$$

where  $\theta$  is the freezing-point lowering, or the boiling-point raising,  $\nu$  is the number of molecules formed per molecule of solute,  $\lambda$  is a constant = 1.858, and  $m$  is the molality (mols per 1000 g. water).

*Boiling-Point Raising.*—Randall and Adams<sup>4</sup> have used Equation 1 for all the available data for aqueous solutions of electrolytes. At the boiling-point  $\lambda$  has the value 0.5125, but this value varies slightly with the barometric pressure.

*Vapour Pressure Lowering.*—For the other experimental methods the divergence function  $h$  of Lewis and Randall was generalised by Randall and White,<sup>5</sup>

$$h = 1 + (55.51 \ln a_1)/(\nu m) \quad . \quad . \quad . \quad (2)$$

For vapour pressure lowering we substitute for  $\ln a_1$ ,

$$\ln a_1 = - \frac{p_1^0 - p_1}{p_1^0} - \frac{1}{2} \left( \frac{p_1^0 - p_1}{p_1^0} \right)^2 - \dots, \quad (3)$$

where  $p_1^0$  is the vapour pressure of the pure solvent and  $p_1$  is the vapour pressure of the solution.

*Osmotic Pressure.*—For osmotic pressure we substitute for  $\ln a_1$ ,

$$\ln a_1 = - \frac{1}{RT} \int_{P^0}^P \bar{v}_1 dP \quad . \quad . \quad . \quad (4)$$

where  $R$  is expressed in c.c. atmos.,  $P^0$  is the pressure on the solvent in the standard state,  $P$  is the pressure on the solvent in osmotic equilibrium with

<sup>2</sup> Ref. 1 (b) pp. 288, 348.

<sup>3</sup> A quantity  $\phi$  identical in value with  $1 - j$  was called the osmotic coefficient by Bjerrum (*Z. Elektrochem.*, **24**, 321 (1918)). The function  $j$  is a property of the solvent.

<sup>4</sup> Randall and Adams, unpublished.

<sup>5</sup> Randall and White, *J. Amer. Chem. Soc.* **48**, 2514 (1926).

the solution,  $(P - P^0)$  is the osmotic pressure, and  $\bar{v}_1$  is the partial molal volume of the solvent. The value of the integral is found by plotting  $\bar{v}_1$  as ordinate, the osmotic pressure as abscissa, and taking the area under the curve to the pressure measured. Whence,

$$h = 1 - (55.51 \times \text{Area}) / (82.07 \text{ } \nu m T) \quad (5)$$

Or, if the solution is dilute, we may take  $\bar{v}_1$  as constant and equal to the molal volume, whence

$$h = 1 - 12.185 (P - P^0) / (\nu m T) \quad (\text{approx.}) \quad (6)$$

*Dew-Point Lowering.*—Randall, McBain, and White<sup>6</sup> reduced the dew point lowering to the equivalent vapour pressure and then used Equation 3.

The distribution and electromotive force measurements give  $a_1$  or  $\ln a_1$  which can be substituted directly in Equation 2.

*Non-Electrolytes.*—In the case of non-electrolytes Lewis and Randall assumed  $h/m$  or  $j/m$  to approach constancy in the dilute solutions. There are no reliable data to test this assumption. The values of the function are not very large, but within the limits of the experimental error it has been verified by Randall<sup>7</sup> for the freezing-point data, by Randall and Adams<sup>7</sup> for the boiling-point data, and by Randall and Batchelder<sup>7</sup> for the osmotic pressure data. Bury<sup>8</sup> has deduced the limiting value of  $j/m$  at  $m = 0$ , by showing that it is equal to the negative of the slope of the curve of  $\theta/m$  plotted against  $\theta$  (B plot of Lewis and Randall). Bury's device is especially valuable as it uses the data in the more concentrated solutions, which are relatively the most accurate, as an aid in determining the limit at  $m = 0$ .

Determinations by these methods can be plotted with  $j/m$  or  $h/m$  against  $m$  on the same piece of paper, or they may be plotted on transparent paper and superimposed for the purpose of aiding in the selection of the most probable value.

The value of the activity coefficient is then given by

$$\log \gamma' = - \frac{j}{2.303} - \frac{1}{2.303} \int_0^m \frac{j}{m} dm + 0.00025 \int_0^m \frac{\theta}{m} d\theta - 55.51 \int_0^m \frac{1}{m} dx \quad (7)$$

where the value of the first integral is the area under the curve of  $j/m$  against  $m$ . The value of the second integral is small except in concentrated solutions. The value of the last integral, which depends upon the heat of dilution, is also small. These are fully discussed by Lewis and Randall. In the case of the  $h$  function the second and third integrals do not appear, and the value of the activity coefficient is at the temperature of the measurements.

*Dissociable Substances and Electrolytes.*—Randall and White<sup>9</sup> have shown that the values of  $j/m^{\frac{1}{2}}$  or of  $h/m^{\frac{1}{2}}$  for strong electrolytes when plotted against  $m^{\frac{1}{2}}$  will approach limiting values at  $m = 0$ , which are the same for each valence type. This limit may be obtained empirically or from the Debye and Hückel<sup>10</sup> theory which requires a slightly different limit for each temperature owing to a change in the dielectric constant of the water. For electrolytes, therefore, we plot  $j/m^{\frac{1}{2}}$  or  $h/m^{\frac{1}{2}}$  against  $m^{\frac{1}{2}}$  and obtain the activity coefficient from the equation,

$$\log \gamma' = - \frac{j}{2.303} - \frac{2}{2.303} \int_0^m \frac{j}{m^{\frac{1}{2}}} dm^{\frac{1}{2}} + \frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} d\theta - \frac{55.51}{\nu} \int_0^m \frac{1}{m} dx \quad (8)$$

<sup>6</sup> Randall, McBain, and White, *J. Amer. Chem. Soc.*, **48**, 2517 (1926).

<sup>7</sup> Unpublished. All the available data have been studied.

<sup>8</sup> Bury, *J. Amer. Chem. Soc.*, **48**, 3123 (1926).

<sup>9</sup> (a) Randall, *J. Amer. Chem. Soc.*, **48**, 2514 (1926); (b) Randall and White, *Ref. 5*.

<sup>10</sup> Debye and Hückel, *Physikal. Z.*, **24**, 185 (1923).

where the first integral is the area under the curve of  $j/m^{\frac{1}{2}}$  and the others are the same as those in Equation 7.

We are thus able to use the same plot to obtain the activity coefficient from measurements by any of the methods which measure the activity of the solvent. We may also compare this plot with that of similar salts by superimposition. If the substance is not a typical strong electrolyte, as an alkali nitrate, or barium nitrate or sulphuric acid,<sup>11</sup> then the plot of  $j/m^{\frac{1}{2}}$  will rise above the curve of other salts of the same type in dilute solution, but the curve will approach the same limit, at  $m = 0$ . If the electrolyte is only moderately strong, as in the case of cadmium chloride, the rise in the dilute end may amount to a decided peak in the curve. In general, if the salt is highly hydrated in solution then the  $j/m^{\frac{1}{2}}$  curve is low and the values of the activity coefficient are high. For salts of about the same degree of hydration, the weaker salts, or those having an ionic diameter less than the distance of nearest approach of the ions,<sup>12</sup> will have curves lying above the curves of the stronger salt.

### Activity Coefficients of Aqueous Solutions from Determinations of the Activity of the Solute.

The activity coefficient as determined from the activity of the solvent at various temperatures may be corrected to any other temperature by aid of the values of the partial molal heat content and capacity, and the results shown by a plot of  $\log \gamma$  against the square root of the ionic strength,  $\mu^{\frac{1}{2}}$ . We shall show that the results of the measurements by all other methods may be transformed so that  $\log \gamma$  plus a constant may be plotted on the same scale against the square root of the ionic strength. Then by superimposing all the curves the best value of the constant in each case can be determined and the several curves averaged.

**Electromotive Force.**—From the electromotive force of cells without liquid junctions in which the electrodes react in such a way as to form in solution the substance whose activity is desired, we may write

$$\log \gamma - \frac{E^0}{(0.00019844 \nu T)/N} = - \frac{E}{(0.00019844 \nu T)/N} - \log m_{\pm} \quad (9)$$

where  $E$  is the measured electromotive force,  $\nu$  the number of ions formed from each molecule of dissolved substance,  $N$  the number of equivalents of electricity per molecule of solute formed,  $m_{\pm}$  the stoichiometric mean molality, and  $E^0$  is the standard *E.M.F.*, or the *E.M.F.* when the ions of the solute are at unit activity. The value of the constant is to be obtained by reference to the  $\log \gamma$  vs.  $\mu^{\frac{1}{2}}$  plot. Of course, a primary extrapolation to  $m = 0$  can be made, using the theoretically required slope at the axis as an aid. The standard *E.M.F.*,  $E^0$ , equals  $\text{const.} \times (0.00019844 \nu T)/N$ .

In concentration cells without liquid junctions the following equation is used:

$$\log \gamma + \text{const.} = - \frac{E}{(0.00019844 \nu T)/N} - \log m_{\pm} \quad (10)$$

where  $m_{\pm}$  is the mean molality of the ions at the varied concentrations. In making the plot against  $\mu^{\frac{1}{2}}$ ,  $\log \gamma + \text{const.} = - \log m_{\pm}'$ , where  $m_{\pm}'$  is the fixed concentration, is also used as one of the points. The constant when found is really  $-(\log m_{\pm}' + \log \gamma')$ .

<sup>11</sup> Randall and Scott, *J. Amer. Chem. Soc.*, **49**, 647 (1927).

<sup>12</sup> See Bjerrum, *Det. Kgl. Danske Videnskab Selskab Math.-fys. Medd.*, **7**, No. 9 (1926).

*Vapour Pressure of the Solute.*—The activity of the solute is proportional to the fugacity of the solute in the gas, or, as a first approximation, proportional to the partial pressure of the solute. Hence we find  $\log a_2 = \log p + \text{const.}$ , or

$$\log \gamma + \text{const.} = (1/\nu) \log p - \log m_{\pm} \quad . \quad . \quad (11)$$

*Distribution Ratios.*—If the activity of the solute is proportional to the mol fraction of the solute in a second solvent, then

$$\log \gamma + \text{const.} = (1/\nu) \log n_2 - \log m_{\pm} \quad . \quad . \quad (12)$$

or, in general, if  $\gamma_u$  is the activity coefficient of the solute in the second phase, then

$$\log \gamma + \text{const.} = (1/\nu) \log (\gamma_u n_2) - \log m_{\pm} \quad . \quad . \quad (13)$$

The constant is the logarithm of the distribution ratio at infinite dilution.

*Solubility of Salt in a Mixture of Electrolytes.*—The activity coefficient is proportional to the reciprocal of the mean molality of the ions of a saturated solution of a moderately soluble salt in water, for since  $a_2$ , the activity of the salt, is constant (solid phase present),

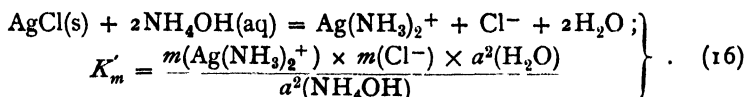
$$\log a_2 = \log (m_{\pm} \gamma)^{\nu} \quad . \quad . \quad (14)$$

and

$$\log \gamma + \text{const.} = \log (1/m_{\pm}) \quad . \quad . \quad (15)$$

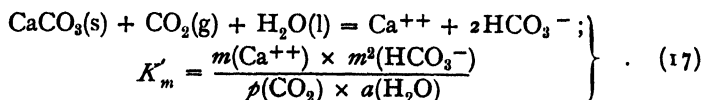
If the salt whose ions are added have the same characteristics, *i.e.* activity coefficient, as the saturating salt the activity coefficient curve of the saturating salt would be continued without a break, but if the added salt has different characteristics there will be a break. We therefore plot the reciprocal of the mean molality against the square root of the ionic strength. By comparison of the curves obtained with the curves for various electrolytes which we would expect to have activity coefficients of about the same values as those of the saturating salt, we are able to obtain the value of the proportionality factor or constant.<sup>13</sup>

*The Equilibrium Constant of a Reaction.*—If we consider a reaction in which only pure solids, liquids, gases or weak electrolytes and equivalent amounts of positive and negative ions are formed from solids, liquids, gases or weak electrolytes, we may obtain the activity coefficient of the dissolved salt in a way similar to that of moderately soluble salts. Consider a reaction such as



which has been studied by Randall and Halford<sup>14</sup>

or



which has been studied by Randall and Tamele.<sup>15</sup> The equilibrium constant is written so that only one mol of the salt being considered is formed. The activities of the solids are constant; those of the weak electrolytes can

<sup>13</sup> Randall and Vietti (unpublished) have examined all the available measurements.

<sup>14</sup> Randall and Halford, unpublished.

<sup>15</sup> Randall and Tamele, unpublished.

be determined from their vapour pressure, distribution ratio, or, as a first approximation, may be taken equal to the molality, if the solution is dilute. The activities of the gases are approximately equal to their pressure in atmospheres, or the fugacity can be found. The activity of the water is easily estimated to within a few tenths of a per cent. The activities of the ions are equal to the activity coefficient times their molality. If the stoichiometric molality of the ions and the activity of the other substances are substituted in the equilibrium expression it is seen that the activity coefficient is given by the equation,

$$\log \gamma + \text{const.} = (1/\nu) \log K'_m \quad . \quad . \quad . \quad (18)$$

The plots of  $\log \gamma + \text{const.}$  and of  $\log \gamma$  against  $\mu^{\frac{1}{2}}$  are now superimposed, and by the aid of similar plots of the activity coefficients of other salts of similar type the best values are selected. We have thus been able to compare data determined by the various methods. Some of these methods give data that are more reliable in one range than in another, but the average result obtained by this procedure is the best that can be obtained.

*Interpolation of Activity Coefficients.*—A modification of an equation of Brönsted's<sup>16</sup> has been suggested by Randall and Breckenridge<sup>17</sup>

$$(\log \gamma)/\mu^{\frac{1}{2}} = A + B\mu^{\frac{1}{2}} + C\mu + \dots \quad . \quad . \quad . \quad (19)$$

in which A, B and C are constants. A plot of  $(\log \gamma)/\mu^{\frac{1}{2}}$  against  $\mu^{\frac{1}{2}}$  is nearly a straight line for strong electrolytes, but for moderately strong electrolytes there is a minimum near the dilute end corresponding to the maximum referred to in discussing the  $j/m^{\frac{1}{2}}$  against  $m^{\frac{1}{2}}$  curves. The intersection on the axis is at A, which corresponds to the slope of the  $\log \gamma$  against  $\mu^{\frac{1}{2}}$  curve near  $m = 0$ .

### Summary.

Methods of calculating the activity coefficient of the solute from that of the solvent are suggested in which the results from all the different methods are brought into the same plot. ( $j/m$  vs.  $m$  and  $h/m^{\frac{1}{2}}$  vs.  $m^{\frac{1}{2}}$  plots.)

The results of the previous methods and those from measurements which give the activity of the solute are correlated in such a way that the plots may be superimposed and the best average values selected. ( $\log \gamma + \text{const.}$  vs.  $\mu^{\frac{1}{2}}$  plots.)

A method of interpolating the activity coefficients of strong electrolytes is suggested. ( $\log \gamma)/\mu^{\frac{1}{2}}$  vs.  $\mu^{\frac{1}{2}}$  plots.)

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<sup>16</sup> Brönsted, *J. Amer. Chem. Soc.*, **45**, 2998 (1923)

<sup>17</sup> Randall and Breckenridge, *ibid.*, **49** (1927).

# THE ELECTRONIC THEORY OF VALENCY, PART V. THE MOLECULAR STRUCTURE OF STRONG AND WEAK ELECTROLYTES (a) COMPLETE IONISA- TION.

BY T. MARTIN LOWRY.

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## 1. The Theory of Complete Ionisation.

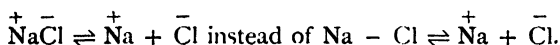
The theory of complete ionisation had its origin in a physico-chemical study of the properties of solutions ; but it was very soon adopted by physicists as an explanation of the high symmetry of the crystal-structures revealed by the X-ray analysis of metallic salts, since this could not be accounted for on the traditional theory that the ions of the salt were united into molecules. The new theory has had a large measure of success in both fields of study, since, on the one hand, the conductivity of solutions of ordinary metallic salts has been calculated for the first time by means of a rationally deduced formula, which is valid up to a concentration of perhaps  $N/100$  ; on the other hand, many of the physical properties of crystals, such as their linear dimensions and angles, heat of formation, elasticity, refractive index and infra-red absorption, have been calculated successfully on the assumption that the crystals are aggregates of ions of varying degrees of "hardness," which are drawn together by the electrostatic attraction between their opposite charges, but are also repelled from one another with a force varying inversely as (say) the 6th to the 35th power of the distance. On the other hand, the theory of complete ionisation (which cannot be expected to "have it both ways") fails to cover the behaviour of those weak electrolytes which obey Ostwald's dilution Law, just as completely as the latter law failed to cover the behaviour of highly-dissociated metallic salts. Again, although many of the properties of solid ionic aggregates, such as rock salt or calcite, have been predicted successfully from fundamental data, all attempts to predict the dimensions and behaviour of the carbonate ion itself have failed, since this does not behave as a mere aggregate of carbon and oxygen ions. The object of the present paper is therefore to determine the boundaries of the region within which the theory of complete ionisation is valid, to find out the factors which make it inoperative in so many cases, and in particular to study the chemical significance of the classification of electrolytes as "strong" and "weak." The applications of similar considerations to the study of crystal-structure will form the subject of a subsequent communication.

In both cases the principal argument put forward will be that, although the ions of a salt are generally prevented from neutralising their opposite electric charges by factors which find their simplest expression in the "octet" rule, there are many cases in which this inhibition does not operate, with the result that the ions can be converted into real molecules, as distinguished from mere aggregates of ions, by the neutralisation of their opposite charges with formation of a chemical "bond." These two groups of compounds correspond broadly with the "strong" and "weak" electrolytes ; but the two methods of classification cannot be expected to lead to identical

results. Thus, on the one hand, a salt which consists entirely of ionic aggregates may be placed under conditions which are so unfavourable to the independent migration of the ions as to bring it within the group of "weak electrolytes;" and, on the other hand, the bond which holds the positive and negative radicles together in a covalent molecule may be so weak as to interfere but little with the disruption of the molecule into ions, with the result that a compound of the second type may exhibit the behaviour of a strong electrolyte.

## 2. Electrolytic Dissociation of Strong Electrolytes.

A "strong electrolyte" means, in the first instance, nothing more than a substance which has a high electrolytic conductivity, *e.g.*, in aqueous solutions. In the language of Arrhenius' theory, such a substance was said to have a large "coefficient of ionisation;" but this term has no longer any real meaning when applied to a salt which is 100 per cent. ionised even in the solid state. We can, however, still interpret the decrease of equivalent conductivity in strong solutions as being due, at least in part, to the formation of electrically-neutral doublets, which play the part of molecules, just as in the vapour of the salt. We need therefore only modify Arrhenius' equation to the extent of writing



The "degree of dissociation" of the doublets then has still a perfectly definite physical meaning, even if it cannot be calculated directly, as was formerly supposed, from the simple equation  $\alpha = \Lambda/\Lambda_\infty$ . Moreover, since the readiness with which neutral doublets of oppositely charged ions are formed by the mutual attraction of their electrostatic charges must vary with the linear dimensions of the ion, with the dielectric constant and other properties of the solvent, and with the extent to which the naked ion becomes hydrated or solvated in solution, as well as with the temperature at which the association and dissociation of the ions takes place, there is ample scope, even in the theory of complete ionisation, for variations in the "degree of dissociation" of different salts, either in solution or in the fused state.

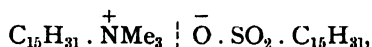
(a) *Ionisation of Strong Electrolytes in Solution.*—Is it possible, then, for a completely ionised salt to behave as a "weak electrolyte" and exhibit a low "coefficient of ionisation" or, more accurately, a low "degree of dissociation" of the pre-existing ions? The answer is undoubtedly "Yes," provided always that the conditions under which this effect is theoretically possible can be realised in practice.

Of these conditions the most obvious has reference to the nature of the solvent. Thus Hartley<sup>1</sup> has shown that, in the case of  $N/500$  KI, the ratio  $\Lambda/\Lambda_\infty$  falls from 0.98 in water to 0.90 in methyl alcohol, 0.81 in ethyl alcohol and 0.77 in acetone, although his solutions were all so dilute that  $1 - \alpha$  was still proportional to the square root of the concentration as required by the theory of complete ionisation. If then we accept the general validity of Walden's rule, that *a dissolved salt gives a definite value for  $\Lambda/\Lambda_\infty$  at a dilution which is inversely proportional to the cube of the dielectric constant of the solvent*, it follows that we should be able to repress the dissociation of the ions to any desired extent by dissolving the salt in a medium of low dielectric-constant.

<sup>1</sup> *Nature*, Feb. 26, 1927, 119, 323.

At this point, however, a fresh difficulty presents itself, since the majority of metallic salts are insoluble except in media which possess marked ionising properties; in particular, most of these compounds are completely insoluble in media, such as benzene or cyclohexane, where the dielectric constant is low enough to compel the salt to behave as a weak electrolyte. Walden has, indeed, put forward a definite rule, according to which *the coefficient of ionisation of a salt is approximately constant for saturated solutions in any anhydrous solvent*. Thus in the case of tetraethylammonium iodide, we should not expect to find any solution in which the "coefficient of ionisation" is much below 50 per cent., since saturated solutions in a dozen different solvents (but excluding water and all other solvents in which the solubility is more than 1 gram-molecule in 2500 c.c.) gave values for  $\alpha = \Lambda/\Lambda_\infty$  which were almost constant at 0.48. We may therefore conclude that only in exceptional cases will it be possible to prepare a solution of a strong electrolyte in which the coefficient of ionisation is so small as to be negligible, and that this effect, when it occurs, will probably be due to some special chemical relationship between the solvent and the solute, which enables the solute to dissolve, but without any marked disruption of the ions.

Such an effect might be looked for in Reychler's trimethylcetyl-ammonium cetylsulphonate



in which the single polar valency in the middle of so long a chain of atoms might very well remain almost undetected. Thus, whilst the 30 carbon atoms in the two hydrocarbon chains should suffice to make the compound soluble in hydrocarbon solvents, these solvents need not necessarily be so drastic in their action as to tear the two ions apart. Fortunately, however, this phenomenon can be observed in much simpler compounds. Thus, sodium oleate at a dilution of 100 litres gives the following equivalent conductivities in water and in methyl, ethyl, and amyl alcohols

$\text{H}_2\text{O}$	$\text{CH}_3\text{OH}$	$\text{C}_2\text{H}_5 \cdot \text{OH}$	$\text{C}_6\text{H}_{11} \cdot \text{OH}$
$\epsilon = 81.7$	$\epsilon = 35.4$	25.4	15.9
$\Lambda_{100}^{18} = 30.09$	$\Lambda_{100}^{25} = 0.0052$	0.0018	0.0002

When sodium oleate is dissolved in *water*, the "hydrophilous" sodium ion compels the "anhydrophilous" oleate ion to follow it into aqueous solution, where it functions as the "ionic micelle" of a "colloidal electrolyte." In the alcohols, on the other hand, and especially in amyl alcohol, the oleate radical appears to drag a reluctant sodium ion into solution in *an organic solvent, in which the salt behaves for all practical purposes as a non-electrolyte*.

Walden, however, has gone a great deal further in studying the abnormal conductivities of salts in hydrocarbons and in their halogen derivatives.

Thus, by a suitable choice of radicals, in salts such as  $\text{N}^+(\text{C}_6\text{H}_{11})_4\bar{\text{I}}$ , he has been able to obtain solutions of reasonable strength in a dozen of the least promising solvents, including benzene and toluene, methyl iodide, methylene and ethylene chlorides, chloroform and carbon tetrachloride. In every case, the salt-solution showed an appreciable conductivity, the values for  $\Lambda_{20}^{25}$  varying from 0.0140 in carbon tetrachloride to 1.57 in chloroform and 9.51 in methylene chloride; but the equivalent conductivities were abnormal in that they generally fell to a minimum value at some intermediate dilution,

from which there was not only the usual increase on dilution, but an equally striking increase on passing to more concentrated solutions. The "degree of dissociation" was obviously small and in some cases almost negligible, so that the "salt" was behaving quite clearly as a "weak electrolyte" in all these solvents. Neutralisation of the ionic charges, however, would appear to be even more difficult than usual, in view of the fact that the positively-charged nitrogen of the tetra-amylammonium ion is separated from the negatively-charged halogen ion by a permanent hydrocarbon "atmosphere" containing 20 atoms of carbon. The small conductivity of these solutions then suggests that the salt must be present predominantly in the form of neutral ionic doublets, rather than as freely dissociated ions. The formation of these doublets also appears to afford a sufficient explanation of the different absorption-coefficients which Hantzsch observed<sup>2</sup> when quaternary ammonium salts of this type were dissolved in organic solvents instead of in water, since we need not suppose that the absorption-coefficients of the ionic doublet must necessarily be identical with those of the aqueous ions.

Attention may also be directed to the fact that, whilst solutions of phosphorus pentabromide and antimony pentabromide in liquid bromine exhibit a marked conductivity,<sup>3</sup> the equivalent conductivity decreasing with dilution just as in the case of the "abnormal" conductivities cited above, potassium bromide and tetramethylammonium iodide, as well as tribromoacetic acid, behave as insulators in this solvent (Walden).

(b) *Ionisation of Fused Salts.*—Since considerations of limited solubility do not apply in the case of fused salts, it is of special interest to enquire what is known in reference to the magnitude of the "coefficients of ionisation" under these conditions. It has been generally assumed that the calculation of these coefficients is impossible, since it cannot be done either by Arrhenius' method, which depends on measuring the conductivity of the salt at different stages of dilution with a solvent, or by van't Hoff's method, which implies a knowledge of the osmotic pressure of the salt in solution. A formal solution of the problem is possible, however, in the case of fused silver chloride at 600° C., for which the relevant data are all known, namely:

Molecular weight	$M = 143.34$
Density	$\delta = 5.267 - 0.0092t = 4.715 \text{ at } 600^\circ$
Specific conductivity	$\kappa = 4.48 \text{ at } 600^\circ$
Viscosity	$\eta = 0.01606 \text{ at } 603^\circ$

The normality of the fused salt is  $4.715 \div 143.34 = 32.9N$ ; and the equivalent conductivity is therefore  $\Lambda = 4.48 \div 0.0329 = 136$ . The limiting value for the conductivity at infinite dilution in aqueous solution is given by the sum of the ionic mobilities as  $54 + 65 = 119$ ; if, therefore, a proportional allowance is made for an increase of viscosity from 0.01056 to 0.01606, the corresponding limiting value for the fused salt would be  $\Lambda_\infty = 119 \times 0.01056 \div 0.01606 = 78$ . The equivalent conductivity of a completely ionised salt can, however, also be calculated, without making use of the value for aqueous solutions, by means of Walden's relation,  $\Lambda_\infty \eta_\infty \sqrt{M} = 11.15$ , which has been verified for six salts in 29 non-aqueous solvents, as well as for two "anhydrous" salts in aqueous solution. For silver chloride this relation gives  $\Lambda_\infty = 11.15 \div 0.01606 \div 12 = 58$ .

These two methods of calculation concur in giving a maximum conductivity for completely dissociated silver chloride,  $\text{AgCl} \rightarrow \text{Ag}^+ + \text{Cl}^-$ ,

<sup>2</sup> *Ber.*, 1919, 52, 5444.

<sup>3</sup> Plotnikow, *Z. physikal. Chem.*, 1904, 48, 228.

which is only about half as great as the values found experimentally. It has been suggested, and the idea has found widespread acceptance, that the exceptional mobility of the ions  $\overset{+}{\text{H}}$  and  $\overset{-}{\text{OH}}$  in aqueous solutions is due to the fact that they are *the ions of the solvent*. This idea is at least plausible

TABLE I.—EQUIVALENT CONDUCTIVITY OF TETRA-AMYLAMMONIUM IODIDE IN ORGANIC SOLVENTS AT 25°.

Chloroform, $\text{CHCl}_3$ $\epsilon = 4.95$	$v = 5$ $\Lambda = 3.185$	10.0 2.45	20.0 1.57	50.0 0.760	100 0.478	
	$v = 50$ $\Lambda = 0.725$	100 0.454	200 0.352	300 0.339 Min.	450 0.340 Min.	600 0.388
Methylene chloride, $\text{CH}_2\text{Cl}_2$ $\epsilon = 8.3$	$v = 20$ $\Lambda = 9.51$	40 9.34 Min.	60 9.47	120 10.44	240 12.26	480 15.16
Carbon tetrachloride, $\text{CCl}_4$ $\epsilon = 2.18$	$v = 2.5$ $\Lambda = 0.0340$	5 0.0245	7.5 0.0216	10 0.0199	20 0.0140	
Methyliodide, $\text{CH}_3\text{I}$ $\epsilon = 7.1$	$v = 50$ $\Lambda = 1.420$	100 1.250	150 1.180	200 1.186	400 1.324	600 1.518
Ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$ $\epsilon = 9.4$	$v = 20$ $\Lambda = 4.20$	40 3.78	80 3.63 Min.	160 3.91	320 4.64	640 5.95
Ethylene chloride, $\text{C}_2\text{H}_4\text{Cl}_2$ $\epsilon = 9.3$ to 10.5	$v = 20$ $\Lambda = 9.52$	40 10.34	80 11.73	160 13.82	320 16.58	$\infty$ 74
Acetylene tetrachloride, $\text{C}_2\text{H}_2\text{Cl}_4$ $\epsilon =$	$v = 20$ $\Lambda = 3.740$	30 3.771	40 3.804	60 3.942	120 4.317	
Acetylene tetrabromide, $\text{C}_2\text{H}_2\text{Br}_4$ $\epsilon = 7.1$	$v = 50$ $\Lambda = 0.149$	100 0.130	150 0.127 Min.	200 0.135		
Propyl chloride, $\text{C}_3\text{H}_7$ $\epsilon = 7.7$	$v = 20$ $\Lambda = 2.64$	40 2.37	60 2.31	80 2.19	160 2.18 Min.	320 2.32
Allyl chloride, $\text{C}_3\text{H}_5\text{Cl}$ $\epsilon = 7.3$	$v = 60$ $\Lambda = 2.50$	120 2.20	180 2.15 Min.	240 2.23	480 2.52	
Benzene, $\text{C}_6\text{H}_6$ $\epsilon = 2.26$	$v = 0.75$ $\Lambda = 0.243$	1.125 0.372	1.50 0.391 Max.	2.25 0.363	3.00 0.323	
	$v = 2.50$ $\Lambda = 0.356$	3.75 0.300	5.00 0.256	10 0.139	20 0.0448	30 0.0207
Toluene, $\text{C}_7\text{H}_8$ $\epsilon = 2.31$	$v = 1.275$ $\Lambda = 0.315$	2.55 0.298	3.82 0.244	5.1 0.204	10.2 0.108	20.4 0.0344
Benzylchloride, $\text{C}_7\text{H}_7\text{Cl}$ $\epsilon = 6.4$	$v = 40$ $\Lambda = 0.464$	100 0.456	200 0.446 Min.	300 0.531	400 0.612	
$\text{NEt}_4\text{I}$ in water $\epsilon = 80$	$v = 32$ $\Lambda = 92.4$	64 98.2	128 102.3	256 105.7	512 109.9	1024 112.9

in the case of water, where it might be supposed that the exceptional mobility of  $\overset{+}{\text{H}}$  (in the form of  $\text{OH}_2^+$ , since  $\overset{+}{\text{H}}$  cannot persist as a separate entity), depended in part on the transfer of a naked proton from one complex to another, without necessarily involving the migration of the whole of the oxonium ion; but it is not valid even in the closely related

case of liquid ammonia, where  $\overset{+}{\text{H}}$  (in the form of  $\overset{+}{\text{NH}}_4$ ) and  $\overset{-}{\text{NH}}_2$  are less mobile than  $\overset{+}{\text{K}}$  and  $\overset{+}{\text{Tl}}$ ; and there is no reason why it should be true in the case of a completely ionised salt, where it is difficult even to suggest a theoretical justification for it. It therefore appears more likely that the high conductivity of fused silver chloride may be due to the presence of something analogous to the "ionic micelle" in a colloidal electrolyte, *i.e.*, to complex aggregates of ions carrying multiple electric charges, since these would have the effect of increasing both the viscosity and the electrolytic conductivity of the melt. Such aggregates might be formed by an incomplete destruction of the crystal lattice and it may be supposed that the conductivity of a fused salt is determined very largely by the character of the aggregates that persist when the crystalline salt is melted.

From this point of view it is of interest to notice that all fused salts are not good electrolytes, even when the theory of valency indicates that they must be completely ionised. Thus, leaving out weak electrolytes such as  $\text{SnCl}_4$  and  $\text{HgCl}_2$ , where covalent molecules appear to be formed from the metal and the halogens, the values

$$\Lambda^{70} = 0.0009, \Lambda^{100} = 0.0050$$

recorded by Walden for the molten hydrobromide of dimethyl-aniline, present a remarkable contrast with the values

$$\Lambda^{600} = 4.48, \Lambda^{800} = 4.98$$

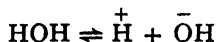
for silver chloride. In this compound we must either suppose that the fused solid breaks up into electrically neutral doublets,  $[\overset{+}{\text{NHPhMe}}_2 \mid \overset{-}{\text{Br}}]$ , in which the oppositely-charged ions cling together, just as they must do in a salt-vapour of normal vapour-density and, therefore, do not migrate in opposite directions under the influence of a small electro-motive force; or we must postulate the existence of some subtle type of bond, which binds the ions into a molecule of such an unstable character that it is unable to persist in aqueous solution (compare Hantzsch's hypothetical pseudo-ammonium halides). Until, however, the existence of such molecules has been proved, it is simpler to admit that a salt, even if it is completely ionised in the crystalline state, will not become a good electrolyte when fused, unless the lattice is resolved into oppositely-charged fragments. If the cleavage of the lattice on fusion tends predominantly to produce neutral ionic aggregates like those which are formed on vaporisation, the conductivity of the fused salt may be reduced to such an extent as to give rise to the properties of a typical "weak electrolyte." This effect, it is clear, is most likely to appear in salts which are easily vaporised, *i.e.*, which break down readily into volatile neutral doublets.

### 3. Hydrolysis.

It is an interesting and novel feature of the theory of complete ionisation that it very largely destroys the meaning of the term "hydrolysis." Thus an equation such as



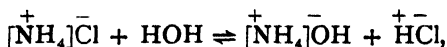
becomes a mere paraphrase of the equation:



unless we admit that the theory of complete ionisation breaks down in the case of one or both of the products.

## 514 STRUCTURE OF STRONG AND WEAK ELECTROLYTES

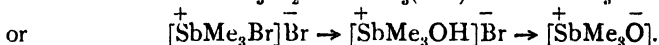
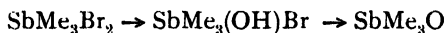
This can always be admitted in the case of the acid, since all hydrogen compounds exist predominantly in a covalent form. A more curious case is afforded by ammonium chloride,



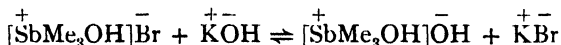
where the acid is so strong that the proportion of covalent hydrogen chloride is too small to produce an appreciable vapour-pressure, but where the base is quite weak. In this case, therefore, hydrolysis depends on the conversion of ammonium hydroxide into a covalent compound. This may take place, as Latimer and Rodebush have suggested,<sup>4</sup> through the weak

linkage of a bivalent hydrogen atom  $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 \cdot \text{H} \cdot \text{O} \cdot \text{H}$ ; but a far more obvious method is by eliminating the hydroxyl ion as a covalent molecule of water  $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$ . In the latter case we reach the curious conclusion that the *hydrolysis* of the salt of a weak ammonium base (which is then a thermal dissociation into which water does not enter directly,  $\text{NH}_4^+\text{Cl}^- \rightleftharpoons \text{NH}_3\text{aq} + \text{HClaq}$ ) would actually depend on a *dehydration* of the hydroxide.

A similar example of "hydrolysis by dehydration" is afforded by the quinevalent compounds of phosphorus, arsenic, and antimony.<sup>5</sup> Thus trimethylstibine dibromide can be hydrolysed in two stages as follows:—



In the first stage hydrolysis can take place in the normal way, by an interchange of Br and OH, since the hydroxyl-ion of the base can be fixed by the quadricovalent antimony, giving rise to a product which can be isolated in the form of an oxy-bromide  $\text{Br}^+[\text{SbMe}_3 \cdot \text{O} \cdot \text{SbMe}_3]\text{Br}^-$ ; but, since the equation,



has no meaning, from the point of view of the theory of complete ionisation, the second stage of the hydrolysis must depend on a direct removal of HBr, giving rise to an oxide, which can be isolated without difficulty, instead of to a dihydroxide.

### Summary.

(a) Compounds in which neutralisation of the ionic charges is prevented by the laws of valency generally behave as "strong electrolytes" in solution. Badly-conducting solutions can, however, be obtained by dissolving a salt in a medium with a low dielectric constant, when abnormal variations of conductivity with dilution are generally observed.

(b) Many fused salts are good conductors, giving values for the "coefficient of ionisation" which may be above 100 per cent., perhaps as a result of the formation of multiply-charged ionic aggregates. Other fused salts, however, are poor conductors, probably because the crystal-lattice breaks down into neutral ionic doublets on fusion.

(c) The term "hydrolysis" has no significance, from the point of view

<sup>4</sup> *J. Am. Chem. Soc.*, 1920, **42**, 1431; cf. Moore and Winnill, *J. Chem. Soc.*, 1912, 101, 1675.

<sup>5</sup> Hantzsch and Hibbert, *Ber.*, 1909, **40**, 1513.

of the theory of complete ionisation, unless the hydrogen or hydroxyl ion of water can be fixed by one of the ions of the salt, with formation of a covalent compound.

*University Chemical Laboratory,  
Cambridge.*

## A NOTE ON THE ACTIVITY OF HYDROGEN ION IN MIXED SOLVENTS.

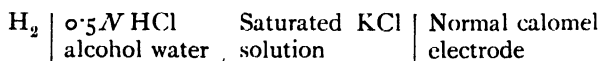
BY HORACE MILLET.

Whilst the activity or thermodynamic concentration of ions has been closely studied by several investigators using aqueous solutions, more recently non-aqueous solutions have been employed with a view to determining the influence of the solvent environment on activity. As a contribution towards the solution of this problem, the writer has determined the hydrogen ion activity of hydrochloric and picric acids in ethyl alcohol water mixtures using the electromotive force method for the necessary determinations.

### Experimental.

1. *Activity of Hydrogen Ion in Ethyl Alcohol Water Mixtures Containing Hydrochloric Acid.*—In the first place we shall deal with the determination of the hydrogen ion activity of 0.5*N* HCl in alcohol water mixtures. The determinations have been carried out at two temperatures (25° C. and 30° C.) and also in presence of sucrose, the range of alcohol water mixtures extending from 0 to 90 per cent. by volume of alcohol.

The hydrogen ion activities have been measured by the ordinary hydrogen electrode by setting up cells of the type



and the usual precautions were taken for preventing the flow of hydrogen gas from altering the concentration of the solution in the cell by previously passing the gas through several wash bottles containing the solution in question.

In order to avoid oxidation of the alcohol, the platinum electrode had only a slight deposit of platinum black.

The hydrogen ion activities were calculated from the formulæ

$$\pi_{25^\circ} = 0.2820 + 0.059 \log a \text{ at } 25^\circ \text{ C.}$$

and

$$\pi_{30^\circ} = 0.2868 + 0.060 \log a \text{ at } 30^\circ \text{ C.}$$

The absolute value of the normal calomel electrode was taken to be 0.5648 volt<sup>1</sup> at 25° C. and 0.5682 volt at 30° C. Saturated solutions of potassium chloride have been used as intermediate liquids for the purpose of annulling the liquid-liquid potentials. It is not altogether certain, however, that this procedure eliminates completely the liquid-liquid potentials.

In Tables I. and II. are given the data obtained for 0.5*N* HCl at 25° C.

<sup>1</sup> Moran and Lewis, *J. Chem. Soc.*, **121**, 1615 (1922).

## 516 ACTIVITY OF HYDROGEN ION IN MIXED SOLVENTS

and 30° C. in ethyl alcohol water mixtures together with the results when 10 per cent. sucrose at 25° C. and 7·5 per cent. sucrose are present at 30° C.

TABLE I.

ACTIVITY OF HYDROGEN ION IN ALCOHOL WATER MIXTURES CONTAINING 0·5N HCl.

Temperature.	Number of c.cs. Alcohol in 100 c.cs. Solution.	Number of grms. of Alcohol in 100 grms. of Solution.	Mean E.M.F. observed in Volts.	Activity of Hydrogen Ion.
25° C.	0	0	0·3073	0·3843
	10	8·04	0·3081	0·3727
	25	20·6	0·3100	0·3459
	40	33·3	0·3143	0·2914
	50	42·8	0·3183	0·2513
	60	52·7	0·3204	0·2305
	75	68·7	0·3192	0·2416
	80	75·0	0·3178	0·2552
	90	86·8	0·3078	0·3770
30° C.	0	0	0·3062	0·3861
	25	20·5	0·3097	0·3375
	40	33·6	0·3135	0·2917
	50	42·8	0·3160	0·2651
	55	47·5	0·3177	0·2483
	60	52·5	0·3182	0·2436
	75	68·4	0·3173	0·2522
	90	86·8	0·3080	0·3603

TABLE II.

ACTIVITY OF HYDROGEN ION IN ALCOHOL WATER MIXTURES CONTAINING 0·5N HCl IN PRESENCE OF SUCROSE.

Temperature.	Sucrose.	Number of c.cs. of Alcohol in 100 c.cs. Solution.	Number of grms. of Alcohol in 100 grms. of Solution.	Mean E.M.F. observed in Volts.	Activity of Hydrogen Ion.
25° C.	10	0	0	0·3040	0·4373
	—	25	22·2	0·3080	0·3741
	—	40	36·1	0·3126	0·3125
	—	50	46·1	0·3149	0·2857
	—	55	50·7	0·3160	0·2738
	—	60	56·4	0·3163	0·2707
	—	70	68·3	0·3150	0·2848
	—	75	74·7	0·3118	0·3225
30° C.	7·5	0	0	0·3037	0·4249
	—	20	17·1	0·3082	0·3575
	—	40	35·3	0·3122	0·3067
	—	45	40·2	0·3130	0·2970
	—	50	45·0	0·3137	0·2895
	—	55	50·4	0·3140	0·2860
	—	60	55·8	0·3136	0·2900
	—	70	66·4	0·3125	0·3033
	—	75	69·0	0·3117	0·3126

2. *Activity of Hydrogen ion in Ethyl Alcohol Water Mixtures containing Picric Acid.*—In this section we shall deal with the determination of the hydrogen ion activity of picric acid at different concentrations in alcohol water mixtures but more particularly with mixtures rich in alcohol.

In the first place, it was found that the ordinary method of measurement

by means of the hydrogen electrode as described earlier was rendered invalid with solutions of picric acid. In order to overcome this difficulty use was made of the quinhydrone electrode developed by Biilman.<sup>2</sup> However, owing to the varying solubility of quinhydrone in alcohol water mixtures it was necessary to evaluate  $E_0$  for the mixtures required. This was accomplished by repeating some of the previous measurements for HCl but using a quinhydrone electrode. The values of  $E_0$  thus obtained for 25° C. are given in Table III.

TABLE III.

Number of c.cs. of Alcohol in 100 c.cs. Solution.	$E_0$ .
0	0.9784
10	0.9825
20	0.9867
40	0.9944
50	0.9968
60	0.9988
70	1.0010
80	1.0016
90	1.0031
100	1.0045

Using the quinhydrone electrode and cells of the type

Picric acid, alcohol-water quinhydrone	Saturated KCl solution	Normal calomel electrode
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measurements have been made of the hydrogen ion activity of picric acid at two concentrations (0.00909*N* and 0.004545*N*) in alcohol water mixtures rich in alcohol, all the determinations being carried out at 25° C.

As in these cases we were employing solvents mostly rich in alcohol, especial care was taken to ensure the absence of water in the alcohol used for preparing the mixtures.

The results of the above-mentioned determinations are given in Table IV.

**Discussion of Results.**—In the first series of results given in Tables I. and II. inclusive, for HCl in alcohol water mixtures it will be observed that the hydrogen ion activity passes through a minimum for a mixture containing about 60 per cent. by volume of alcohol. This will be seen from Fig. 1 where the data in Table I. are given graphically.

The composition of the solvent at this point, namely 30 per cent. grammoles of alcohol, thus corresponds approximately with that of the complex  $C_2H_5OH \cdot 3H_2O$  which contains 25 per cent.

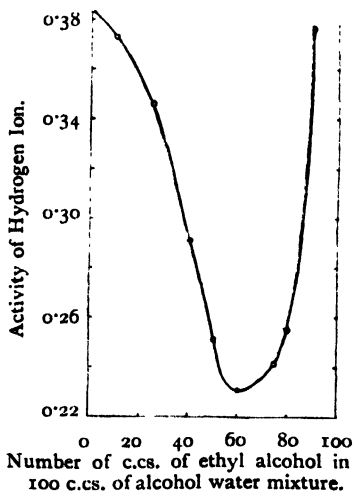


FIG. 1.—Activity of hydrogen ion in alcohol water mixtures containing 0.5*N* HCl at 25° C.

<sup>2</sup> Biilman, *Ann. Chim.*, 75, 102 (1921).

TABLE IV.

ACTIVITY OF HYDROGEN ION IN ALCOHOL WATER MIXTURES CONTAINING PICRIC ACID AT 25° C.

Picric Acid ( $N \times 10^{-3}$ ).	Number of grms. of Alcohol in 100 grms. of Solution.	Number of grm. moles of Water Per Litre.	Mean <i>E.M.F.</i> observed in Volts.	Activity of Hydrogen Ion.
9.09	100	0.00	0.3784	0.09144
	99.95	0.02	0.3773	0.08757
	99.9	0.04	0.3768	0.08588
	99.8	0.08	0.3760	0.08324
	99.6	0.16	0.3737	0.07620
	99.2	0.32	0.3690	0.06334
	98.5	0.64	0.3625	0.04934
	97.4	1.28	0.3485	0.03473
	94.25	2.56	0.3320	0.01524
	88.8	5.12	0.3085	0.00626
	78.5	10.24	0.2912	0.00333
	68.4	15.36	0.2915	0.00339
4.54	100	0.00	0.3741	0.07730
	99.9	0.04	0.3727	0.07318
	99.8	0.08	0.3716	0.07010
	99.6	0.16	0.3693	0.06409
	99.2	0.32	0.3644	0.05294
	98.5	0.64	0.3546	0.03611

grammoles of alcohol. The minimum point is slightly displaced by sucrose and, from the cases chosen, the concentration of alcohol at the minimum point is about 58 per cent. by volume. The direction of the displacement rather suggests an increased hydration of the sucrose in the alcohol water mixtures.

One must be cautious in drawing conclusions based on the formation of an alcohol water compound, as it is well known that many alcohol water compounds have been postulated from the behaviour of the physical properties of alcohol water mixtures. In spite of this, it is believed in the present case that the above result constitutes evidence for the existence of a compound having the above composition.

The reason for such a conclusion may be briefly outlined. If the hydrogen ion activities of HCl in alcohol water mixtures are reduced to unit hydrogen ion concentration (as determined from conductivity data), it is found that the

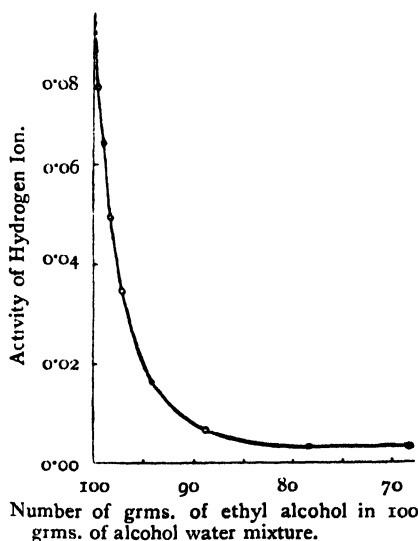


FIG. 2.—Activity of hydrogen ion in alcohol water mixtures containing 0.00909*N* picric acid at 25° C.

minimum still remains but is now a little nearer to the point corresponding with the alcohol water compound indicated.

Had the minimum been removed in this way, we might have inferred that one of the constituents of the mixture, say the alcohol, was not acting as a solvent for hydrogen ion. As, however, this minimum does persist with these "corrected" activities it seems reasonable to assume that this peculiar behaviour is due to the presence of the compound  $C_2H_5OH \cdot 3H_2O$ .

When we turn to the data for the hydrogen ion activity of picric acid in alcohol water mixtures it must be remembered that we are dealing with mixtures having a high concentration of alcohol and where the influence of alcohol water compounds should be much less marked.

From the results given in Table IV. and from Fig. 2, it will be seen that as the concentration of water is gradually increased from zero, the hydrogen ion activities fall very rapidly. This behaviour can be compared with the similar alteration of the mobility of the hydrogen ion in alcoholic solutions containing small amounts of water as the concentration of water is increased.

Taking the data of Goldschmidt<sup>3</sup> for  $\Lambda_\infty$  of HCl in alcohol containing traces of water as giving approximately the values of the corresponding mobility of the hydrogen ion, it is interesting to compare the values of  $\frac{a_H}{U_H}$ .

for the case of picric acid. The values of the ratio  $\frac{a_H}{U_H}$  are given in Table V.

TABLE V.

COMPARISON OF ACTIVITY AND MOBILITY OF HYDROGEN ION IN ALCOHOL WATER MIXTURES CONTAINING PICRIC ACID AT 25°C.

Picric Acid ( $N \times 10^{-3}$ ).	Concentration of Water in moles Per Litre.	Activity of Hydrogen Ion, $a_H$ .	Mobility of Hydrogen Ion, $U_H$ .	$\frac{a_H}{U_H} \cdot 10^4$ .
9.09	0.00	0.0914	89	10.3
	0.02	0.0876	78	11.2
	0.04	0.0859	72	11.9
	0.08	0.0832	63	12.8
	0.16	0.0762	58.3	13.1
	0.32	0.0633	53	12.0
	0.64	0.0493	49.2	10.0
4.545	0.00	0.0773	89	8.69
	0.04	0.0732	72	10.2
	0.08	0.0701	65	10.8
	0.16	0.0641	58.3	10.9
	0.32	0.0529	53	9.9

It will be seen from the foregoing that there is a parallelism between the behaviour of the hydrogen ion activities and the corresponding mobilities in alcoholic solutions containing small amounts of water.

As the influence of intersolvent compounds can be neglected in the present instance where we are dealing with the addition of minute quantities of water to alcohol, it is believed by the writer that the rapid decrease in the hydrogen ion activity of picric acid produced in this way might possibly be due to the hydration of hydrogen ion, which, it is assumed, would be ineffective electrochemically. The possibility of such hydration would be favoured by the low dielectric constant of the mixtures considered. Furthermore, the behaviour of the hydrogen ion activities can be accounted for fairly satisfactorily on this basis, as will be briefly described.

<sup>3</sup> Goldschmidt, *Z. f. Elektrochem.*, **20**, 475 (1914).

The formation of a hydrated form of hydrogen ion  $H^+ \cdot H_2O$ , will be governed by the relationship

$$a_{H^+} \times a_{H_2O} = K \cdot a_{H^+ \cdot H_2O}$$

where  $a_{H^+}$ ,  $a_{H_2O}$  and  $a_{H^+ \cdot H_2O}$  are activity terms and  $K$  is a constant.

Restricting our treatment to a region in the neighbourhood of absolute alcohol where the dielectric constant will be sensibly constant, the writer has calculated the values of  $a_{H^+ \cdot H_2O}$ . The values of the activity of the hydrogen ion hydrate  $H^+ \cdot H_2O$  pass through a maximum for a mixture containing 94 per cent. by weight of alcohol.

It is assumed that the decrease in the hydrogen ion activity in alcohol brought about by the addition of a small quantity of water is proportional to the amount of hydrated hydrogen ion present.

In Table VI. are given the values of the hydrogen ion activities calculated in this way and are compared with those actually observed.

The value enclosed in brackets was used to determine the required proportionality constant.

TABLE VI.

HYDROGEN ION ACTIVITY OF PICRIC ACID IN ALCOHOL CONTAINING SMALL QUANTITIES OF WATER AT 25° C.

Picric Acid ( $N \times 10^{-3}$ ).	Number of grms. of Alcohol in 100 grms. of Solution.	$a_{H^+ \cdot H_2O}$ .	Activity of Hydrogen Ion.	
			Calculated.	Observed.
9.09	100	—	0.0914	—
	99.95	0.00438	0.0893	0.0876
	99.9	0.00859	0.0871	0.0859
	99.8	0.0167	0.0831	0.0832
	99.6	0.0305	(0.0762)	(0.0762)
	99.2	0.0507	0.0661	0.0683
	98.5	0.0789	0.0520	0.0493
4.545	100	—	0.0773	—
	99.9	0.00732	0.0694	0.0732
	99.8	0.0140	0.0703	0.0701
	99.6	0.0256	0.0645	0.0641
	99.2	0.0424	0.0561	0.0529
	98.5	0.0570	0.0484	0.0361

It is clear from the above that provided the amount of water added to the alcohol is not very great, the alteration in the hydrogen ion activity thus produced can be accounted for fairly satisfactorily if it is assumed that part of the hydrogen ion becomes hydrated.

Attention will now be drawn to an interesting empirical relationship which is found to hold for the hydrogen ion activities of HCl in alcohol water mixtures. The relationship referred to is

$$k = \frac{aD^2}{\Lambda_v}$$

where  $a$  is the activity coefficient of the hydrogen ion,  $\Lambda_v$  is the equivalent conductivity,  $D$  is the dielectric constant of the medium, and  $k$  is a constant.

The application of the relation just given to some of the hydrogen ion activities obtained by the writer will be found in Table VII. The dielectric constants used are those obtained by interpolation from Nernst's

data at 20° C., and the values for the equivalent conductivity of HCl in alcohol water mixtures at 25° C. are those given by Kablukov.<sup>4</sup>

TABLE VII.  
ALCOHOL WATER MIXTURES CONTAINING HCl AT 25° C.

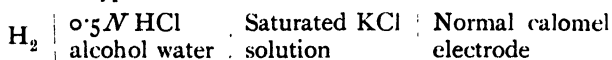
HCl (N).	Number of c.cs. of Alcohol in 100 c.cs. of Solution.	Activity Coefficient of Hydrogen Ion, $a_{\pm}$	Dielectric Constant, D.	Equivalent Conductivity $\Lambda_{\pm}$	$k = \frac{\alpha D^2}{\Lambda_{\pm}}$
0.5	0	0.769	81	353	14.3
	10	0.745	75	290	14.5
	20	0.710	69.3	233	14.6
	40	0.583	58.5	140	14.3
	50	0.503	52.9	104	14.5
	60	0.461	47	74	14.0
	70	0.468	41	54	14.6
	80	0.510	35.6	37	17.4
0.01	0	0.989	81	407	15.0
	10	0.902	75	330	15.4
	25	0.796	66.4	230	15.3
	40	0.679	58.5	155	15.0
	50	0.564	52.9	120	13.1

For the cases considered in the two tables above the relation  $k = \frac{\alpha D^2}{\Lambda_{\pm}}$  holds fairly well. However, it cannot be claimed to be generally applicable and breaks down when we consider, for example, purely alcoholic solutions of electrolytes.

### Summary.

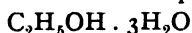
1. Determinations are given for hydrogen ion activities in ethyl alcohol water mixtures containing 0.5*N* HCl at 25° C. and 30° C. and also in presence of sucrose.

The measurements were obtained from electromotive force measurements using cells of the type



2. Hydrogen ion activities are recorded for picric acid in alcoholic solutions containing small quantities of water. Cells involving the use of a Biilman electrode were employed.

3. The minimum activity obtained with HCl is shown to lead one to expect the existence of an alcohol water compound, namely,



4. The rapid fall observed with the hydrogen ion activities in mixtures rich in alcohol when the water content is gradually increased is shown to be similar in behaviour to the corresponding fall in hydrogen ion mobilities. The effect is believed to be connected with the hydration of hydrogen ion, and a calculation is made of the hydrogen ion activities which would be expected on this basis. They are found to agree with the corresponding observed values.

<sup>4</sup> Kablukov, *Z. physik. Chem.*, **4**, 433 (1889).

5. An empirical relationship, namely,

$$k = \frac{\alpha D^2}{\Lambda_0}$$

is found to connect the hydrogen ion activity coefficients  $\alpha$  for HCl in alcohol water mixtures with the values of the corresponding equivalent conductivities  $\Lambda_0$  and the dielectric constants  $D$  of the medium.  $k$  of course is a constant. The relationship has only a limited application.

The above measurements were carried out in connection with an investigation of reaction velocity in alcohol water mixtures.

The writer's thanks are due to the Department of Scientific and Industrial Research for a maintenance grant.

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## THE EFFECT OF ONE SALT ON THE SOLUBILITY OF ANOTHER IN ETHYL ALCOHOL SOLUTION. PART I.

BY F. E. KING AND J. R. PARTINGTON.

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The experiments described in the present communication are the first of a series made with the object of determining the effect of one salt on the solubility of another in ethyl alcohol solutions. The treatment will not be confined to very dilute solutions, nor to those which at the moment seem to be of theoretical interest. The study will include concentrated as well as dilute solutions. In the experiments now described the influence of lithium iodide, and of sodium thiocyanate, on the solubility of sodium iodide in ethyl alcohol at 25° has been investigated, and conductivities and viscosities of one set of solutions (sodium iodide and sodium thiocyanate) have been determined in addition to the solubility data.

No application of the conductivities has been made in the present paper since time did not permit the extension of the measurements to the solutions containing lithium iodide, nor the completion of the necessary calculations. So far as we are aware the present work is the first which has been made with the object of studying the solubility relations of electrolytes in non-aqueous solution, and we intend, as stated above, to extend this work in a number of directions.

### Experimental.

#### *Preparation of Materials.*

(1) *Sodium Iodide and Ethyl Alcohol.*—The preparation and purification of these substances have been described in a short paper on the solubility of sodium iodide in ethyl alcohol.<sup>1</sup>

(2) *Sodium Thiocyanate.*—Sodium thiocyanate was prepared by the decomposition of pure ammonium thiocyanate with caustic soda prepared from

<sup>1</sup> *J. Chem. Soc.*, 128, 20, 1926.

sodium. A concentrated solution containing these substances was evaporated in a porcelain dish until all the ammonia had been driven off and crystallisation began. The sodium thiocyanate was then recrystallised from distilled water and 96 per cent. alcohol. A small amount of the salt was dried in an electric oven at  $130^{\circ}$  and was analysed by precipitation as silver thiocyanate, which was weighed. Two determinations gave the theoretical percentage of CNS, 71.64.

(3) *Lithium Iodide*.—The method of preparation of lithium iodide was identical with that of the sodium salt, with the exception that it was first necessary to free the lithium carbonate from traces of sodium salts by washing with boiling distilled water. By repeated crystallisation almost white crystals of  $\text{LiI} \cdot 3\text{H}_2\text{O}$  were obtained which were partly dehydrated by phosphorous pentoxide in a vacuum desiccator. To dehydrate the iodide completely fairly strong heating is necessary,<sup>2</sup> and on account of the ease with which the compound oxidises, it is necessary to carry out this operation in an inert gas, or in a vacuum. The method finally adopted was that due to W. E. S. Turner and Bissett,<sup>3</sup> in which the iodide is heated electrically in a vacuum desiccator over phosphorous pentoxide. Analysis by gravimetric silver estimations gave iodine 94.77 per cent. (Theory 94.83 per cent). The salt was free from iodate, which Simmons and Pickett,<sup>4</sup> have shown to be the chief product of oxidation, and errors in weighing out the samples for analysis, due to the extreme deliquescence of the iodide, probably account for the slight difference between the observed and theoretical percentages of iodine.

#### *Solubility Determinations.*

The method of preparing the solutions of the sodium iodide-thiocyanate mixtures differed only slightly from that previously described for the pure iodide.<sup>1</sup> The materials were introduced into the larger tube (A, Fig. 1 in the paper quoted) of the solubility apparatus, and after immersion overnight in a thermostat at  $25^{\circ}$ , during the whole of which time the solution was stirred, the excess of solid was allowed to settle and the colourless saturated solution drawn off into the tube B as previously described.

On the addition of alcohol to mixtures of sodium and lithium iodides, however, the lithium salt was oxidised on account of the rise in temperature produced by its large heat of solution, and a dark brown solution containing free iodine resulted. A solution of the required amount of lithium iodide in alcohol was therefore prepared by placing the dehydrated salt in an empty desiccator, previously dried out by phosphorous pentoxide, together with a quantity of pure alcohol contained in a separate vessel. The desiccator was exhausted, and the alcohol vapour began to condense on the iodide, this process continuing until all the alcohol had been transferred. The solution thus produced was poured over an excess of sodium iodide in the solubility apparatus and the determination carried out as before.

In order to obtain the solubilities in terms of c.c. of solution from those in terms of grams of solvent, an accurate value for the density of the solution must be known. This could not be obtained by the use of the ordinary pipettes previously employed, and the filter tube was therefore ground to fit a pycnometer, shaped in the form of a V to facilitate filling. The rubber stopper was removed from the top of the filter tube, the pycnometer was attached and filled by suction. Caps were fitted on the pycnometer which was then placed in the thermostat. After adjustment

<sup>2</sup> Abegg, *Handbuch der anorganischen Chemie*, ii, 1, 130.

<sup>3</sup> *J. Chem. Soc.*, 29, 233, 1913.

<sup>4</sup> *J. Amer. Chem. Soc.*, 49, 701, 1927.

to the correct volume the pycnometer was dried, suspended on the balance, and allowed to attain the temperature of the balance case. No precipitation of the salts resulted from this treatment and it was unnecessary to replace the pycnometer in the thermostat (although this precaution was generally taken) before going on with the solubility determinations.

The bulk of the solution in the pycnometer was run into an evaporating flask previously described, and its weight determined. The flask was then electrically heated with a current of pure dry hydrogen passing through it. This process was repeated with a second sample of the solution.

The weighed residues of approximately 2.5 to 3 gms. were then dissolved in water and made up to 200 c.c. for analysis. Although direct analysis of chloride or bromide in the presence of thiocyanate is possible, this method cannot be used with mixtures of iodide and thiocyanate, since the iodide is also decomposed by the methods used to remove the thiocyanate. The solutions were therefore analysed indirectly. Measured volumes of the aqueous solution were precipitated with acidified silver nitrate solutions, the precipitated silver salts dried at 130°-135°, and weighed. This was afterwards replaced by the more convenient volumetric method. The results obtained by both methods when applied to the same solutions were in good agreement. At first an attempt was made to obtain both iodide and thiocyanate directly. The precipitation of the iodide occurs quantitatively first, and the end-points of the thiocyanate titrations are shown by the disappearance of the red colour due to ferric thiocyanate, produced by the addition of iron alum solution towards the end of the titrations. An external indicator of chlorine water and starch gave the end-points of the iodide titrations, but with solutions of known strength the amounts of iodide indicated by the observed end-points were appreciably lower than the correct values. It was found that the blue colour of starch iodide is destroyed by sodium thiocyanate and although at first there is sufficient soluble iodide to give a colour, the thiocyanate interferes with the titration as the iodide concentration becomes small, producing a false end-point. Complete titration with silver nitrate solution, however, forms a good method for indirect estimation of a mixture of sodium iodide and sodium thiocyanate, when taken in conjunction with the weight of the mixed salts.

If  $x$  and  $y$  are the amounts of sodium iodide and sodium thiocyanate in the experimentally determined weight,  $w$ , of the residue obtained on the evaporation of a weighed amount of alcoholic solution saturated with the former salts, and if  $z$  is the total amount of silver required to titrate the  $x + y$  grams of residue, then

$$x + y = w$$

$$\text{and} \quad \frac{\text{Ag}}{\text{NaI}} \cdot x + \frac{\text{Ag}}{\text{NaCNS}} \cdot y = z, \quad \text{i.e., } 0.7195 x + 1.331 y = z.$$

From these equations the values of  $x$  and  $y$  are found from the experimentally determined values  $w$  and  $z$ .

The indirect method appears to be the most satisfactory for the mixed iodides of sodium and lithium and the determinations were carried out gravimetrically by precipitation of the aqueous solution with silver nitrate. The amounts,  $x'$ ,  $y'$ , of each salt present in the mixture were determined by means of the equations,

$$x' + y' = w'$$

and  $\frac{\text{AgI}}{\text{NaI}} x' + \frac{\text{AgI}}{\text{LiI}} y' = z'$ , *i.e.*,  $1.566 x' + 1.754 y' = z'$ ,

where  $z'$  is the total weight of silver iodide produced from  $w'$  grams of the mixed iodides.

### Solubility Data.

TABLE I.—SOLUBILITIES OF SODIUM IODIDE IN PRESENCE OF SODIUM THIOCYANATE.

Solution.	Total Solubility.	NaI.	NaCNS.	Density $D_{40}^{25^\circ}$ .
NaI	42.85 (Mean)	—	—	1.04599
1	42.98	41.81	1.17	1.04223
2	43.11	39.18	3.93	1.03603
3	43.18	36.70	6.48	1.03089
4	43.16	36.25	6.91	1.03050
5	43.26	35.65	7.61	1.02994
NaCNS	20.99	—	—	0.882502

TABLE II.—SOLUBILITIES OF SODIUM IODIDE IN PRESENCE OF LITHIUM IODIDE.

Solution.	Total Solubility.	NaI.	LiI.	Density $D_{40}^{25^\circ}$ .
1	42.79	34.71	8.08	1.04706
2	42.87	29.56	13.31	1.04763
3	43.32	15.57	27.75	1.05606
4	49.98	3.18	46.80	1.09753
5	52.00	2.56	49.44	1.10990
LiI	250.8 (T and B)	—	—	—

The solubilities of sodium iodide in the presence of five different concentrations of sodium thiocyanate, the solubilities of the separate salts, and the densities of these solutions, are given in Table I. All solubility results are expressed in grams of salt per 100 grams of solvent.

Table II. consists of the solubilities of sodium iodide in five different solutions of lithium iodide, together with the densities of the solutions of the mixtures. The value for the solubility of lithium iodide obtained by W. E. S. Turner and Bissett,<sup>5</sup> is included.

In Fig. 1 the amounts of sodium iodide, in terms of grams/100 grams EtOH, in the mixtures have been plotted against the concentrations of the added salts in equivalents/100 grams EtOH. Although a mean value for the solubility of sodium iodide of 42.57 grams/100 grams EtOH has been found it will be seen that experiments 1, 5, 6, 7 and 10 (Solubility of NaI etc., *loc. cit.*), differ but slightly from a mean value of 42.85. If this value for the solubility is assumed, the points representing the solubilities in presence of sodium thiocyanate are in a perfectly straight line. For similar concentrations the curve illustrating the effect of lithium iodide is of the same type, but with higher concentrations the precipitating effect of the iodide is less pronounced.

In Fig. 2 the values of  $\log s/s_0$  are plotted against  $c$ , where  $s_0$  and  $s$  are the solubilities in grams/litre of saturated solution, of sodium iodide alone, and in the presence of an added salt of concentration  $c$  equivalents/litre.

<sup>5</sup> *J. Chem. Soc.*, 103, 1904, 1913.

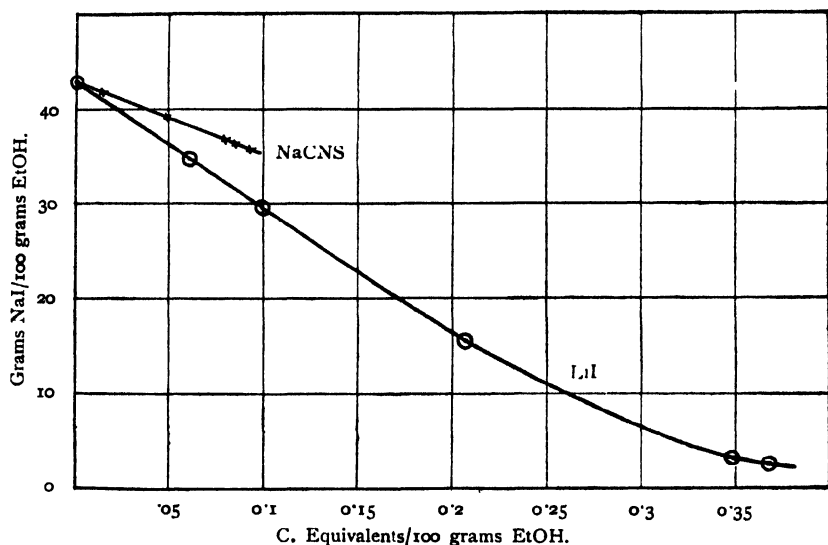


FIG. 1.

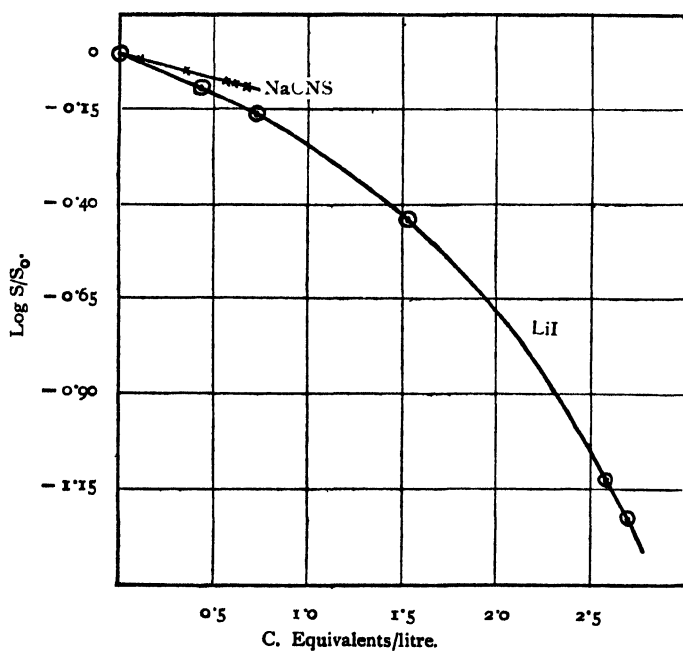


FIG. 2.

Fig. 2 shows that the effect of sodium thiocyanate on the solubility of sodium iodide in these solutions is of the kind usually associated with the salting out effect.<sup>6</sup>

In the case of lithium iodide the effect due to small amounts is of the

<sup>6</sup> K. Linderstrom-Lang, *Compt. rend. trav. lab. Carlsberg*, 15, No. 4, 1, 1924.

same character, the curve being nearly a straight line, but at higher concentrations a pronounced curvature makes its appearance. It is clear that no simple equation such as  $\log s/s_0 = kc$  can account for the salting out effect of lithium iodide over a wide range of concentration. This is to be expected because the equation applies strictly only to solutions of a non-electrolyte. It is, however, interesting that the results for sodium thiocyanate and part of those for lithium iodide can be represented by this equation. The precipitating power of the lithium salt is greater than that of the thiocyanate, and in this connection it is noteworthy that for *aqueous* solutions the lithium salts in general show the greatest precipitating power, while thiocyanates show the least.

### Conductivity and Viscosity Determinations.

A cell, Fig. 3, was used in which the conductivity and viscosity of the same sample of solution could be determined. It consists of a glass tube, A, 18 cms. in length and  $2\frac{1}{2}$  cms. in diameter, sealed at the bottom to a capillary arm, B, near the top of which is a small bulb, C, of approximately 5 c.c. capacity. This is continued in a tube, D, of about  $\frac{1}{2}$  cm. bore having a constriction at E about 2 cms. above the bulb. Two marks, one just below the bulb and the second at the narrowest part of the constriction, form the graduation marks of the viscometer. The top of the cell is closed by means of a glass stopper F, through which pass two tubes sealed to stout circular platinum electrodes at the bottom of the cell. The stopper is continued in a tube, G, of narrow bore which is bent at right angles about 5 cms. above the top of the cell. Just below the stopper is a vertical side arm, H, ground to fit the pyknometer, by means of which the solutions are run into the cell.

The viscosities were determined by means of the method due to Scarpa.<sup>7</sup> By means of a siphon device the pressure on the liquid in the viscometer is reduced by a constant amount, and this constant negative pressure causes the liquid to rise. The time  $t_1$  taken by the top of the liquid column to pass from the lower mark and reach the upper mark is noted, and then the time  $t_2$ , taken in falling under its own weight between the same marks. According to Scarpa the viscosity is proportional to  $t_1 t_2 / (t_1 + t_2)$ , and is independent of the surface tension, density, and amount of liquid, provided that the negative pressure is constant. The apparatus was standardised by means of water, the viscosity of which<sup>8</sup> at 25° was taken as 0.00912 dynes. cm. <sup>-2</sup>. Thorpe and Rodger's value<sup>9</sup> is 0.00891 dynes. cm. <sup>-2</sup>. The former value has been preferred. From this value the proportionality constant for a given negative pressure is obtained. Pure water was introduced from the pyknometer, and the viscometer arm was connected to a 2-way tap by means of which connection with the atmosphere, or the negative pressure apparatus and a water manometer, could be made. The times of ascent under negative pressures of

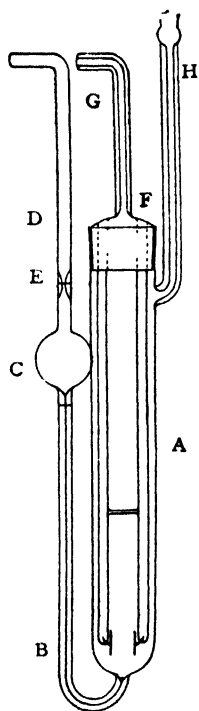


FIG. 3.

<sup>7</sup> *Gazz.*, 40, ii., 261, 1910.

<sup>8</sup> Leroux, *Ann. Physique*, 4, 163, 1925.

<sup>9</sup> *Phil. Trans.*, 185, 397, 1894.

approximately 15, 25, and 35 cms. of water less than atmospheric read off on the water manometer, and the times of fall, were determined. From the viscosity of water the constants for the three pressures were obtained.

The cell was thoroughly washed out with 96 per cent. EtOH until the conductivity of the alcohol appeared constant. It was then emptied, and dry dust-free air passed through until the cell was completely dried. The side arm was closed by a rubber stopper, the cell placed in the thermostat and the viscometer arm connected to the 2-way tap. To prevent the access of moisture to the alcoholic solutions tubes of phosphorous pentoxide and caustic potash were inserted between the tap and the negative pressure device, and similar tubes were connected to the second arm of the 2-way tap and to the tube from the stopper of the cell. The presence of these tubes made no difference whatever in the times of flow of the liquid in the viscometer.

The alcoholic solutions were withdrawn from the solubility apparatus by means of the pycnometer and run into the cell through the side arm, which was then closed. The solution was drawn up into the bulb to moisten the apparatus and to assure that the solution attained the temperature of the thermostat. A standardised circular bridge containing about 20 ft. of wire, calibrated resistance boxes, and the current from a small induction coil were used for the conductivity measurements. To obtain sharp minima the electrodes were lightly platinised. This did not cause any noticeable change in the readings, due to oxidation of the alcohol, the first reading being reproducible after a number of others had been taken.

The negative pressure was then adjusted to one of its constant values and the times of rise and fall of the liquid in the viscometer were taken.

In order to test the apparatus the viscosity of pure ethyl alcohol was determined. The conductivity was found to be too slight for accurate measurement with the existing apparatus, but it was of the order of  $1 \times 10^{-7}$  to  $1 \times 10^{-8}$  [ohms cm.]<sup>-1</sup>. The viscosity was then determined. With the highest negative pressure (about 35 cms. water less than atmospheric) there was a pronounced turbulence in the alcohol, and even with the medium pressure (25 cms. less than the atmospheric) this was still visible. The same statement applies to the calibration liquid, water. It is not surprising therefore, that only the lowest negative pressure (15 cms. water less than atmospheric) gave results in fair agreement with the determinations of other workers. A value of 0.01065 dynes. cm. <sup>-2</sup> for the viscosity of ethyl alcohol was found, which is somewhat lower than Thorpe and Rodger's value of 0.010933 dynes cm. <sup>-2</sup> interpolated for the same temperature. With the higher negative pressures exceedingly low values were obtained, and these were rejected for reasons previously stated. It will be seen that taking only the times of fall, the instrument may be regarded as an Ostwald viscometer, since the volumes of liquid used were the same in all cases. The density of the alcohol had been determined, ( $D_4^{25} = 0.78507$ ), and using the formula  $\eta_1 = \eta_w \delta_1^2 / \delta_w^2$ , the viscosity is found to be 0.01071 dynes. cm. <sup>-2</sup> which is in fairly good agreement with the value obtained by the Scarpa method. However, the results obtained by this latter method should be accepted with caution; if we consider the values of  $\eta$  for the saturated solutions it is seen that they are consistently higher than those obtained by the Ostwald method. For the purpose of correcting conductivity measurements, extremely accurate values are unnecessary.

In determining the ionisation values of the mixtures, the conductivities of the separate salts are required. Dutoit and Rappeport<sup>10</sup> give the mole-

<sup>10</sup> *J. Chim. Phys.*, 6, 545, 1908.

cular conductivity at infinite dilution  $\Lambda_{\infty}$  of sodium thiocyanate in alcohol at  $18^{\circ}$  as 41.6 (Siemens' units), while Dhar and Bhattacharyya<sup>11</sup> have determined the conductivities at several dilutions at temperatures of  $0.2^{\circ}$ ,  $5^{\circ}$ , and  $29.9^{\circ}$ . No measurements at  $25^{\circ}$  appear to have been recorded and the conductivities at dilutions of approximately 10. V, 100. V, and 1000. V were therefore determined in a conductivity cell of ordinary design. The exact concentrations (moles/c.c.) and the conductivities ( $[\text{ohms cm.}]^{-1}$ ) of the three dilute solutions and those of the saturated solution are given in Table III. A. The cube-roots of the concentrations are plotted against  $\Lambda$  in Fig. 4, and it is obvious that the usual extrapolation formula, considered

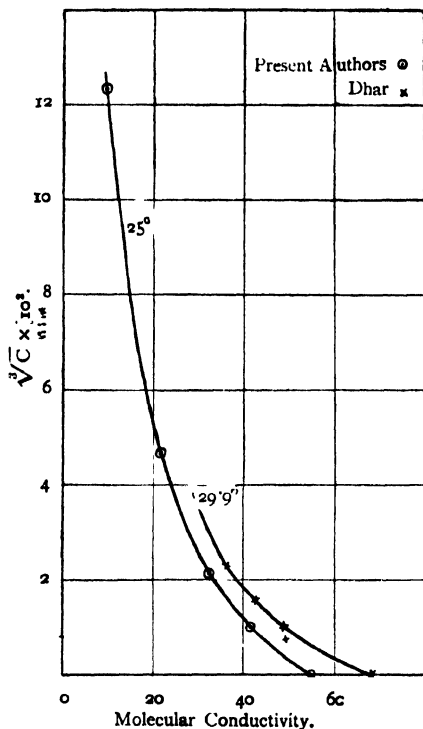


FIG. 4.

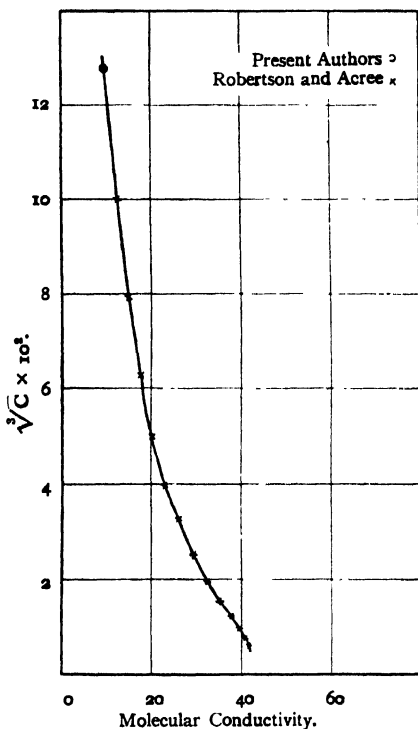


FIG. 5.

adequate by Philip and Courtman<sup>12</sup> for solutions of potassium and tetraethylammonium iodides in various organic solvents, does not apply. Furthermore, the results of Völlmer<sup>13</sup> show that the cube-root formula does not apply generally to electrolytes in ethyl alcohol. If Völlmer's formula,  $\Lambda_{\infty} = \Lambda(1 + A c^{\frac{1}{3}} + B c^{\frac{2}{3}})$  is employed a value for  $\Lambda_{\infty}$  of sodium thiocyanate = 54.83  $[\text{ohms cm.}]^{-1}$ , is obtained.

Dhar's results for  $\Lambda$  at  $29.9^{\circ}$ , plotted in the same way, are included in Fig. 4 for comparison. Extrapolation by means of the Völlmer formula, using the points marked 1, 2 and 3, gave  $\Lambda_{\infty}$  at  $29.9^{\circ} = 68.37 [\text{ohms cm.}]^{-1}$ . When corrected by the temperature coefficient given by Dhar,  $\Lambda_{\infty}$  at  $25^{\circ} = 63.54 [\text{ohms cm.}]^{-1}$  is found. Dutoit and Rapoport's value, similarly corrected to  $25^{\circ}$ , is 49.60  $[\text{ohms cm.}]^{-1}$ .

<sup>11</sup> *Z. anorg. Chem.*, **82**, 257, 1913.<sup>12</sup> *J. Chem. Soc.*, **97**, 1261, 1910.<sup>13</sup> *Ann. Phys. Chem.*, **iii**, 52, 328, 1894.

The viscosities and specific conductivities of the saturated solutions of sodium iodide and sodium thiocyanate, and of the solutions containing thiocyanate saturated with iodide, are given in Table III. B.

TABLE III. A.—MOLECULAR CONDUCTIVITIES OF NaCNS IN ALCOHOL.

Solution.	Concentration (Moles/c.c.).	$\Lambda$ [(ohms cm.) <sup>-1</sup> ].
Saturated . . . . .	$1.888 \times 10^{-3}$	9.50
10 . V. . . . .	$1.0305 \times 10^{-4}$	21.59
100 . V. . . . .	$1.0305 \times 10^{-5}$	32.33
1000 . V. . . . .	$1.0305 \times 10^{-6}$	41.59

TABLE III. B. — THE VISCOSITIES AND SPECIFIC CONDUCTIVITIES OF IODIDE—THIOCYANATE MIXTURES.

Solution,	Specific Conductivity [ohms cm.] <sup>-1</sup> .	Viscosities (Water = 0.00912 dynes cm. <sup>-2</sup> ).	
		(a) Searpa Method.	(b) Ostwald Method.
NaI	$2.050 \times 10^{-2}$	0.02991	0.02878
1	$2.055 \times 10^{-2}$	0.03042	0.02834
2	$2.059 \times 10^{-2}$	0.03147	0.03030
3	$2.061 \times 10^{-2}$	0.03198	0.03048
4	$2.063 \times 10^{-2}$	0.03208	0.03092
5	$2.070 \times 10^{-2}$	0.03182	0.03032
NaCNS	$1.794 \times 10^{-2}$	0.02475	0.02378

In the case of sodium iodide an excellent series of values for the conductivities has been determined by Robertson and Acree,<sup>14</sup> and it was not considered necessary to do more than determine the value for the saturated solution ( $c = 2.094 \times 10^{-3}$ ) in order to complete the series. The results are plotted against the cube roots of the concentrations in Fig. 5 and the value of 9.79 [ohms cm.]<sup>-1</sup> for the saturated solution is included. Robertson and Acree consider that complete dissociation is reached at a dilution of about 4000 V, corresponding to a value for  $\Lambda_{\infty}$  of 41.51 [ohms cm.]<sup>-1</sup>.

All the conductivity values in the present paper are uncorrected for viscosity. In connection with this point Robertson and Acree make the following remarks (p. 389, *loc. cit.*):—

"No method is known at present, however, for doing this, namely correcting the conductivities for viscosity, with certainty. Noyes' method is to multiply the apparent per cent. of ionisation of the salt in a given solution by some power of the ratio of the viscosity of this solution to that of the pure solvent. The power chosen . . . as a first approximation was unity. We believe, however, that this correction is far too large . . . the relation of the viscosities and the conductivities of N/1, N/2 and of N/4 solutions of sodium iodide, . . . at 25° and 35°, for example, are such that if we were to apply Noyes' method we should arrive at the conclusion that the per cent. of ionisation is practically the same for the N/1, N/2 and N/4 solutions of each salt. Such a conclusion is, however, not in harmony with all of the known facts of physical chemistry and certainly is not borne out by our other experimental results. . . . We have therefore contented

<sup>14</sup> *J. physical Chem.*, 19, 413, 1915.

ourselves with the assumption that the ratio  $\mu_0/\mu_\infty$  gives a much closer approximation for  $\alpha$  in our concentrated alcoholic solutions than does the expression  $\mu_0 Z_0/\mu_\infty Z_\infty$  used by Noyes, and we have made all our calculations accordingly."

If the viscosity correction  $\eta/\eta_0$  is applied to the saturated solutions the values for  $\Lambda$  are more than doubled.

Thus $\Lambda$ NaCNS uncorrected	= 9.50 [ohms cm.] <sup>-1</sup>
"corrected"	= 21.1 [ohms cm.] <sup>-1</sup>
$\Lambda$ NaI uncorrected	= 9.79 [ohms cm.] <sup>-1</sup>
"corrected"	= 26.3 [ohms cm.] <sup>-1</sup> .

### Conclusions.

The results obtained indicate that the mutual solubilities of salts in such concentrated solutions depend on more than one effect. Of these the Solubility Product effect is the most interesting, and this can be most easily examined in the case of sparingly soluble salts. We are proceeding with experiments of this nature. Experiments on the *E.M.F.*'s of concentration cells containing salts in ethyl alcohol solution are also in progress.

The cost of the materials used in this investigation has been defrayed by grants from the Chemical Society, and from the Dixon Fund of the University of London, for which the authors wish to express their thanks.

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## PART II. QUANTITATIVE DISCUSSION OF THE SOLUBILITY OF SODIUM IODIDE IN THE PRESENCE OF SODIUM THIOCYANATE.

*(Communicated after the Meeting on 23rd May, 1927.)*

According to the theory of electrolytic dissociation the solubility of a salt is reduced by adding another salt with a common ion. Experiment has generally supported this solubility principle for aqueous solutions, while the work recorded in the first paper of this series has shown it to be true for sodium iodide in alcoholic solutions of lithium iodide and sodium thiocyanate. In discussing the mutual solubilities of salts from a quantitative point of view, it is necessary to assume a law governing the equilibrium of the electrolytes present in the solution, and on this law the values obtained for the concentrations of the un-ionised and ionised parts of the saturating salt will depend. Since the conductivity of a solution is determined by the concentrations of the various ions, a comparison between the observed and calculated conductivities will show to what extent the assumption with regard to the ionisation of the mixed electrolytes is justified.

The conductivities of the sodium iodide-sodium thiocyanate solutions have been calculated from the data for the separate salts by three different methods. Each of these methods is based on one of the three following assumptions:—

(1) The dissociation of each salt is unaffected by the presence of the second salt.

(2) The dissociation of each salt is equal to that which it has when present alone at a concentration equal to the total concentration of the mixture.<sup>1</sup>

(3) The dissociation of each salt is equal to that which it has when present alone in a solution in which its ions have a concentration equal to the concentration of the common ion in the mixture.<sup>2</sup>

It should be emphasised that some doubt exists as to the reliability of the values of the equivalent conductivities of the salts at infinite dilution used in calculating their degrees of ionisation. The curves obtained by plotting the values of  $\Lambda$  against the corresponding values of  $\sqrt[3]{c}$  over the measured range of dilutions are nearly the same for the two salts (Figs. 4 and 5, Part I.), and hence a fairly close agreement between the respective conductivities at infinite dilution is to be expected. At dilutions greater than 1000V., however, the results of Robertson and Acree for sodium iodide, which in this range are not in good agreement with one another, indicate that  $\Lambda$  quickly approaches a limiting value in a finite concentration interval, which is quite different from that which has been calculated for the thiocyanate. If the equivalent conductivities 29.29, 32.25 and 35.07, and the corresponding concentrations are used to solve the Völlmer equation, the conductivity of sodium iodide at infinite dilution is found to be 52.98. The adoption of this value brings the curves for the two salts into nearly identical form throughout the whole range of dilutions, and the values 52.98 and 54.83 for the conductivities of sodium iodide and sodium thiocyanate at infinite dilution have therefore been employed. Nevertheless it must be pointed out that the curvature introduced by the adoption of these numbers is greater than that indicated by graphical methods. It is therefore very probable that the values of  $\Lambda_{\infty}$  are somewhat too high, but in the absence of consistent data for the two salts more trustworthy figures cannot be obtained.

In calculating the specific conductivities of the solutions of the mixed salts by the first method the values of  $\Lambda$  for the separate salts were obtained from the curves shown in Figs. 4 and 5 (Part I.) drawn on a large scale. As in the previous paper no corrections for the viscosities were applied. From the conductivities and the concentrations of the salts in the mixtures the specific conductivities of the solutions were calculated. The results are presented in Table IV.

TABLE IV.

Solubilities.		Equiv. Conductivity.		Spec. Conductivity.		Calculated $K_1 + K_2$ of Mixture.
NaI.	NaCNS.	NaI.	NaCNS.	$K_1$ NaI.	$K_2$ NaCNS.	
20.33	1.052	9.89	21.50	2.010	0.226	2.236
18.91	3.509	10.18	15.95	1.924	0.560	2.484
17.62	5.754	10.47	13.75	1.845	0.791	2.636
17.41	6.136	10.52	13.48	1.831	0.822	2.653
17.01	6.748	10.59	13.15	1.801	0.887	2.688

The column headed Solubilities gives the solubilities of sodium iodide in equivalents  $\times 10^4$  per c.c. of solution in the presence of different concentrations of sodium thiocyanate expressed in the same units.  $K_1$  and

<sup>1</sup> Barmwater, *Z. physik. Chem.*, **28**, 424, 1899; **45**, 557, 1903; **56**, 225, 1906.

<sup>2</sup> Arrhenius, *Z. physik. Chem.*, **2**, 284, 1888; **31**, 218, 1899.

$K_2$  are the separate conductivities  $\times 10^2$  and  $K_1 + K_2$  is the calculated specific conductivity ( $\times 10^2$ ) of the mixture.

In applying the second and third assumptions to the calculation of  $K_1 + K_2$ , it is necessary to know the ionisations of the two electrolytes at concentrations greater than the saturation values in the pure solvent. Table V. shows that these can be extrapolated with fair accuracy from the existing data by means of the Storch dilution formula  $(ca)^n/c(1-a) = K$ . The first two columns contain the concentrations  $\times 10^4$  and the corresponding values of  $\Lambda$  for the respective salts, from which the values of  $100a$ , and of the ion concentrations  $\times 10^4$  given in columns 3 and 4 are derived.

TABLE V.

	$c$ .	$\Lambda$ .	$100a$ .	$\Sigma Ci$ .	$K$ .	$k$ .
Sodium Iodide $n = 1.63$ $\Lambda_\infty = 52.98$	10.00	12.50	23.59	2.359	16.0	0.728
	17.01	10.59	19.98	3.398	16.3	0.849
	17.41	10.52	19.85	3.455	16.4	0.856
	17.62	10.47	19.75	3.481	16.3	0.857
	18.91	10.18	19.20	3.632	16.4	0.864
	20.33	9.89	18.66	3.794	16.1	0.871
	20.94	9.79	18.48	3.868	16.0	0.877
	(22.49)		(18.00)	(4.048)	16.0	0.899
	(24.43)		(17.50)	(4.276)	16.0	0.907
	(26.60)		(17.00)	(4.523)	16.0	0.926
Sodium Thiocyanate $n = 1.54$ $\Lambda_\infty = 54.83$	1.052	21.50	39.21	0.413	27.6	0.266
	3.509	15.95	29.10	1.021	28.8	0.419
	5.754	13.75	25.08	1.443	28.3	0.483
	6.136	13.48	24.59	1.506	28.2	0.492
	6.748	13.15	23.98	1.619	28.4	0.511
	18.88	9.50	17.33	3.272	27.6	0.686
	(20.55)		(16.90)	(3.475)	27.6	0.707
	(22.28)		(16.50)	(3.677)	27.6	0.726
	(24.66)		(16.00)	(3.945)	27.6	0.751
	(27.22)		(15.50)	(4.220)	27.6	0.774
	(30.20)		(15.00)	(4.530)	27.6	0.800
	(33.58)		(14.50)	(4.869)	27.6	0.826
	(37.50)		(14.00)	(5.261)	27.6	0.858
	(42.08)		(13.50)	(5.680)	27.6	0.896

By applying the Storch formula to the known values of  $c$  and  $100a$ , and solving the equations in pairs the exponent  $n$  was found to be 1.63 for sodium iodide and 1.54 for sodium thiocyanate. At lower concentrations, however, the values of  $n$  increased considerably, and the expression cannot be said to represent the behaviour of these electrolytes over a wide range of concentrations with dependable accuracy. For this reason the extrapolation of  $\Lambda$  to infinite dilution by this method was not attempted. At very high concentrations, however, the constancy of  $K \times 10^4$  in the last column but one justifies the adoption of the formula.

From the values of  $n$  and  $K$  the concentrations corresponding to various assumed values of  $100a$  were calculated. For the sake of comparison the values of  $k = (ca)^2/c(1-a)$ , *i.e.* the ordinary mass action equation ( $\times 10^4$ ), are included in the last columns of the two tables.

The values of  $K_1 + K_2$  in Table VI. have been calculated by Barmwater's method. The concentrations of the two salts given in this table are equivalent to the total salt concentrations of the mixtures, and the values of  $100a$  corresponding to these concentrations were obtained from the

graph of  $\epsilon$  against  $\alpha$  using the necessary extrapolated data from the Table V.

The results of the third method of calculation which are based on the isohydric principle are contained in Table VII.

TABLE VI.

Experiment.	Equiv. Concns.		100 $\alpha$ NaI.	100 $\alpha$ NaCNS.	K <sub>1</sub> NaI.	K <sub>2</sub> NaCNS.	K <sub>1</sub> + K <sub>2</sub> .
	NaI.	NaCNS.					
1	2'090	3'865	18'49	13'87	1'991	0'080	2'071
2	2'081	3'850	18'52	13'89	1'856	0'267	2'123
3	2'073	3'834	18'54	13'90	1'731	0'438	2'170
4	2'072	3'833	18'55	13'90	1'711	0'468	2'179
5	2'074	3'835	18'54	13'90	1'671	0'514	2'185

TABLE VII.

Experiment.	$\Sigma$ Cl.	100 $\alpha$ NaI.	100 $\alpha$ NaCNS.	K <sub>1</sub> NaI.	K <sub>2</sub> NaCNS.	K <sub>1</sub> + K <sub>2</sub> .
1	3'901	18'36	16'05	1'977	0'093	2'070
2	3'988	18'13	15'93	1'817	0'306	2'123
3	4'065	17'98	15'57	1'689	0'491	2'170
4	4'078	17'95	15'55	1'656	0'523	2'179
5	4'093	17'91	15'51	1'614	0'573	2'188

In order to obtain the values for the degrees of dissociation of the salts in the mixtures, the ionisation values,  $\alpha$ , were plotted against the ion concentrations,  $\alpha a$ , of the separate salts. A value for  $\alpha a$  was then chosen, and the corresponding ionisations of the two salts were obtained from the graph. This process was repeated until the sum of the values of  $\alpha a$  for the two salts was identical with the assumed value of the ion concentration. The actual values of the total ion concentration,  $\Sigma Ci$ , and of the corresponding ionisations, are presented in the columns 2, 3, and 4 of the table.

If the calculated specific conductivities are compared with the observed values (Table III.B, Part I.), it is obvious that the experimental results are quite opposed to the first assumption. The calculations of  $K_1 + K_2$  are independent of the values of  $\Lambda_\infty$ , and the alterations which a viscosity correction would introduce are comparatively small. It is evident, therefore, that the first supposition leads to results which are considerably higher than those determined experimentally.

The two remaining methods of calculation yield results which are practically identical, and the maximum deviation from the observed values is less than 6 per cent. The effect of a viscosity correction on the calculated figures would only serve to increase them slightly, and so it is concluded that neither Barmwater's method, nor that based on the isohydric principle, accurately represents the conditions existing in these concentrated solutions. The latter method is slightly more accurate, as the following considerations will show. The viscosity correction is greater for the lower values of  $\alpha$  (*i.e.* higher concentrations) for a particular salt, and therefore the values of the specific conductivity due to thiocyanate,  $K_2$ , will be increased to a greater extent in the case of Table VI. than in Table VII. This relative increase of  $K_2$  will be greater than that of  $K_1$  in Table VII. over  $K_1$  in Table VI.,

and so the total increase of  $K_1 + K_2$  will be greater in the results calculated by Barmwater's method.

From the values of  $\alpha$  in the previous table and the solubility data the concentrations ( $\times 10^4$ ) of the ionised and un-ionised fractions in the mixture were calculated (Table VIII.). In the sixth and seventh columns are the concentrations of undissociated sodium iodide ( $\times 10^4$ ) and the values of the solubility product ( $\times 10^7$ ). Both of these quantities decrease markedly on the addition of increasing amounts of sodium thiocyanate although the concentration of the added salt is not large compared with the normal solubility of the iodide. The figures for  $k = [\text{Na}^+][\text{I}^-]/[\text{NaI}]$  given in the last column show that the molecular solubility and the solubility product decrease at approximately the same rate.

TABLE VIII.

Experiment.	$[\text{Na}^+]$ .	$[\text{CNS}^-]$ .	$[\text{I}^-]$ .	$[\text{NaCNS}]$ .	$[\text{NaI}]$ .	$[\text{Na}^+][\text{I}^-]$ .	$k = \frac{[\text{Na}^+][\text{I}^-]}{[\text{NaI}]}$ .
NaI	3.869	—	3.869	—	17.07	1.497	0.877
1	3.901	0.169	3.732	0.883	16.60	1.456	0.877
2	3.988	0.559	3.429	2.950	15.48	1.367	0.883
3	4.065	0.896	3.169	4.858	14.45	1.288	0.891
4	4.078	0.954	3.124	5.182	14.20	1.274	0.892
5	4.093	1.047	3.046	5.701	13.96	1.247	0.893

It is interesting to compare these results with those obtained from similar studies of aqueous solutions. According to the principle of constant molecular solubility the total solubility of a salt in the presence of a second salt can never be less than the concentration of the undissociated part. Arrhenius<sup>3</sup> was the first to show that this statement was untrue, and an examination of the data presented above will show that in the fifth experiment the solubility of sodium iodide has been depressed below the value of  $[\text{NaI}]$  for the saturated solution of the pure salt.

In addition to discrepancies of this kind Noyes and his co-workers,<sup>4</sup> and Hill<sup>5, 6</sup> have found variations in the values of the solubility product. The former have found that the solubility product *increases* on the addition of salts with or without common ions, while according to Hill's experiments on the mutual solubilities of electrolytes without common ions there is a *decrease* in this quantity. Hill has shown, however, that the direction of these changes in the solubility product depends on the dilution law employed in the calculations. The present work is based on assumptions similar to those used by Noyes, but a *decreasing* solubility product has been found. It must be borne in mind, however, that the values in the last table cannot be quantitatively exact, since the poor agreement between the calculated and observed conductivities proves that the underlying assumptions only approximately represent the dissociation equilibria of the salts present in the solutions.

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<sup>3</sup> Z. physik. Chem., **31**, 197, 1899.

<sup>4</sup> J. Amer. Chem. Soc., **33**, 1645, 1911.

<sup>5</sup> Ibid., **32**, 1186, 1910; <sup>6</sup> Ibid., **39**, 218, 1917.

# THE ACTIVITY COEFFICIENTS OF PROTEIN IONS.

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The electric charge or valence of protein particles is a variable, which depends upon the hydrogen ion concentration of the solution and other factors. Although the experimental difficulties in dealing with the proteins are greater than those encountered with the simple strong electrolytes, the protein ions are of interest from the theoretical point of view, because it is possible to study the effects of variations in the valence while the diameter of the ion is kept constant.

The proofs of the constancy of the molecular weight of hæmoglobin will be discussed in detail elsewhere.<sup>1</sup>

There are two points shown by the data in Tables I. and II. which may be considered from the point of view of the inter-ionic attraction theory.

TABLE I.

ISOELECTRIC HÆMOGLOBIN. (VALFENCE  $n_p = 0$  WHEN  $p_H = -\log [H] = 6.8$ .)

Molality. $m_p$ .	Osmotic Coeff. $\xi_p$ .	Activity Coeff. $f_p^*$ .	Ratio. $f_p/f_p^*$ .
·0002	1·02	1·05	·99
·001	1·13	1·28	·98
·002	1·30	1·74	·97
·003	1·52	2·55	·92
·004	1·83	4·23	·86
·005	2·32	8·64	·77

The ratio ( $f_p/f_p^*$ ) given in Table I., column 4, diminishes as the protein concentration increases. This observation is in accordance with the theory, which predicts that the activity coefficient  $f_p$  of the ion at valence 8 should be diminished far more than the coefficient  $f_p^*$  when the valence is zero, when the protein concentration is increased.

The absolute values of the coefficients, however, do not agree with the formulæ of Debye and Hückel, because  $f_p^*$  and  $f_p$  both increase as the protein concentration increases. In their formulæ the free energy of an ion is treated as the sum of two terms, the first of which is equal to the free energy of an ideal gas molecule, and the second is dependent upon the electrical forces. It seems probable that a third term must be added in the case of large ions such as hæmoglobin, the osmotic pressure of which is similar to that which would be given by a non-ideal gas, with a "b" correction 2·5 times the volume of the molecules. According to Van der Waal's, "b" for a gas composed of rigid spheres is four times the volume of the molecules.

The molalities were calculated on the assumptions that the mass of 1 gram. mol. of hæmoglobin was 68,000 when dry and 83,000 including the

<sup>1</sup> Adair, *Proc. Roy. Soc. A.* In press.

TABLE II.

IONISED HÆMOGLOBIN. (VALENCE  $n_p = -8.5$  WHEN  $p_H = 7.8$ .)

Molality. $m_p$ .	Activity Coeff. $f_{ps}$ .	Correction.	Activity Coeff. $f_p$ .
·0002	1·05	1·02	1·03
·001	1·38	1·09	1·26
·002	2·0	1·18	1·69
·003	3·04	1·29	2·36
·004	5·10	1·40	3·64
·005	10·16	1·52	6·70

 $m_p$  = gram mols. hæmoglobin-hydrate per litre of solvent. $g_p = p_{obs}/RTm_p$ . $p_{obs}$  = osmotic pressure measured with collodion membrane at 0° C. $f_p^*$  = activity coefficient of protein salt or protein ion (equal at isoelectric point). $f_{ps}$  = activity coefficient of potassium hæmoglobinate, when the activity coefficients of the diffusible salts are kept constant. $f_p$  = activity coefficient of hæmoglobin ion (valence 8.5).Correction = anti log  $(n_p EF/RT)$ . E = membrane potential.

water of hydration. My original determinations of the molecular weight<sup>2</sup> have been confirmed by the recent measurements of Svedberg and Fåhræus.<sup>3</sup>

In the case of the diffusible components of a protein system, the membrane equilibrium formulæ of Gibbs or the equivalent formulæ of Donnan provide a simple means of deducing activities, but in the case of the non-diffusible component, the problem is more complex, and a brief statement of the theory used for the calculations in Tables I. and II. is given below:

$$vd(P' - P'') = vd p_{obs.} = RT d \ln a_{ps} = RT d \ln m_{ps} f_{ps} \quad (1)$$

where  $v$  is the volume of solvent in litres per gram mol. of protein.  $P'$ , the total osmotic pressure of a protein solution in which the activity of the protein salt varies and the activities of water and of the diffusible salts are kept constant;  $P''$  is the osmotic pressure of a solution of diffusible salts, the activity of each one of which is equal to its activity in the protein solution, and  $p_{obs.}$  is the osmotic pressure measured with a collodion membrane, when the fluid outside the osmometer is of constant composition and the protein concentration is varied inside the membrane.

The "outer fluid" in Table I. contained  $\frac{1}{10}$  mols. of KCl,  $\frac{1}{15}$  mols. of the Sørensen phosphate mixture  $p_H$  6.8. The outer fluid in Table II. contained KCl and the phosphate mixture for  $p_H$  7.8.

The activity coefficient of the protein ions was calculated by means of the formula below:

$$vd p_{obs.} = RT d \ln a_p + n_p F d E = RT d \ln m_p f_p + n_p F d E \quad (2)$$

where  $a_{ps}$  is the activity of protein salt,  $a_p$  = activity of protein ion,  $m_{ps} = m_p$  the mols. of protein or protein ions per litre of solvent, and  $n_p$  = valence of protein ion.

Equations 1 and 2 were integrated by graphical methods and the integration constants were adjusted so that  $f_p$  and  $f_p^*$  were equal to unity when the protein concentration was very small.

<sup>2</sup> *Proc. Camb. Phil. Soc. (Biol.)* I. 75 (1924); *Proc. Roy. Soc., A* 108, 627 and 109; 292 (1925).

<sup>3</sup> *J. Amer. Chem. Soc.*, 48, 430 (1926).

## GENERAL DISCUSSION.

**Professor Fajans** said that Professor Bjerrum's paper had dealt with the disagreement with the theory of Debye and Hückel in the case of heats of dilution, which for many salts were negative instead of, as was theoretically to be expected, positive. He mentioned that according to experiments made in his laboratory by Dr. Lange and Mr. Messner, that difficulty largely disappeared if one worked with sufficiently dilute solutions. The differential calorimeter employed consisted of a Dewar vessel divided by an ebonite plate into two halves, in each of which there were 1000 junctions of a thermo-couple. The sensitivity was  $\frac{1}{100000}$  of a degree or 1/1000 calorie. The initial concentrations of the solutions employed were for uni-univalent salts M/100, for uni-bivalent and bi-bivalent salts M/400. He said that of the results obtained so far at those large dilutions all the heats of dilution measured were positive, in agreement with the theory, and that the order of magnitude of the theoretical values appeared to be correct.<sup>1</sup>

**Professor Porter** was interested in the proposal that the Soret effect was proportional to the change in the square root of the temperature. He had himself put forward a similar view in a paper recently accepted by the Faraday Society (Vol. 23, Part 4, 314). Taking data obtained recently in Professor Donnan's laboratory by Dr. C. C. Tanner, the proposed law was seen to be very closely followed in the case of KCl.

Tanner obtained more than ten times the value for  $\frac{d \cdot \log c}{d \log T}$  quoted by Professor Bjerrum. Tanner's values, however, were so consistent with one another as to justify confidence in their correctness.

**Professor Scatchard** said that it was very interesting to note that Dr. Müller,<sup>2</sup> attacking the problem of the complete Boltzmann expression by a purely mathematical method, obtained nearly the same results as Professor Bjerrum had obtained by physico-chemical methods. However, it seemed very doubtful whether the behaviour of polyatomic ions such as the nitrate and iodate ions should be explained by small size. It must be remembered that the theories so far applied assume ions with spherical symmetry. Lack of such symmetry, like small size, would give a decrease of activity coefficient with increasing ionic concentration, and it was possible that this effect accounted for the behaviour of these ions.

**Dr. J. A. V. Butler** drew attention to a recent paper by T. J. Webb,<sup>3</sup> which was important because it represented a new method of attacking the problem. The Debye-Hückel theory was based on the calculation of the electrostatic forces between ions considered as being in a medium of uniform dielectric constant. The polar nature of the medium was not directly involved. But the dipoles of the medium contributed appreciably to the electric field at any given point. Webb had applied the theory of polarised dielectrics and had calculated the electric work of charging a single ion in a medium as the work done in polarising the medium. The

<sup>1</sup> For further details cf. Lange and Messner, *Bunsengesellschaft, Dresden*, 1927, and *Naturwissenschaften*, 1927, 15, 521.

<sup>2</sup> *Physikal. Z.*, 28, 324 (1927).

<sup>3</sup> *J. Amer. Chem. Soc.*, 1926, 48, 2589.

extension of this method to solutions containing many ions, so as to include interionic effects, would appear to be the direction in which progress might be made.

**Dr. J. N. Pring** (*communicated*) remarked that in his paper Dr. Millet stated that the accuracy of the activity data given would be limited by the presence of a boundary potential between the solvents. Data by other workers on analogous systems made it appear that this boundary potential between the solvents in question was of considerable magnitude. A possible method of making this measurement seemed to be to utilise the principle that apart from the boundary potential the potential of calomel electrodes would be independent of the solvent if saturated solutions were employed.

He suggested that the results obtained and ideas put forward in Dr. Millet's paper should be considered in the light of the somewhat parallel investigation conducted by Lapworth on this subject.<sup>4</sup> A fall in activity or "availability" of hydrochloric acid in alcohol through the presence of water similar to that obtained in Dr. Millet's work was obtained and the values for this fall determined electrically agreed with those calculated from measurements on the relative catalytic activities in organic reactions and from vapour pressure determinations. The results were attributed to the high affinity of the hydron for alcohol whereby the hydrions became more extensively solvated.

**Dr. Millet** said that the adoption of the type of cell suggested by Dr. Pring, for obtaining activity data when using different solvents, might lead to results which were more or less free from the uncertainty due to boundary potentials.

With regard to Dr. Pring's other point it was, of course, known that Goldschmidt<sup>5</sup> favoured the idea that the ionic complex  $H \cdot C_2H_5OH$  was the true catalyst for a number of reactions studied by him and other workers in alcohol water mixtures. He (Dr. Millet), however, was of the opinion that in such media the only ionic complex which was formed by hydrogen ion was that expressed by the formula  $H \cdot H_2O$  and, differing from Goldschmidt, that the true catalyst was unhydrated hydrogen ion. This view was supported, among other things, by the similarity between the reaction velocity data obtained by Burrows<sup>6</sup> for the inversion of sucrose in alcohol water mixtures and the corresponding data he had himself obtained for the activity of hydrogen ion in these same mixtures.

**Dr. J. A. Christiansen** (*communicated later*) remarked that in his treatment of the salt effect on the solubility of non-electrolytes, Professor Scatchard according to formulæ (1), (4) and (6) considered the whole effect as being due to the relative depression of dielectric constant with increasing concentration of the non-electrolyte.

This might be correct for instance with oxygen (fig. 6), but it was certainly not so with egg-albumin (fig. 7). Sørensen and collaborators had shown by direct analytical means<sup>7</sup> that albumen in solution is hydrated to a greater extent than that in the crystalline phase. Consequently, according to the mass-action law,

$$\frac{a_{H_2O}^x}{a_P \cdot x_{H_2O}} = \frac{K}{a_P}$$

<sup>4</sup> *J. Chem. Soc.*, 1915, 107, 857.

<sup>5</sup> Goldschmidt and Uddy, *Z. physikal. Chem.*, 60, 728 (1907); 70, 627 (1910).

<sup>6</sup> Burrows, *J. Chem. Soc.*, 105, 1260 (1914).

<sup>7</sup> *Comptes rendues du Lab. de Carlsberg*, 12, 1, 1917.

(where  $a_p$  and  $a_{p, \times H_2O}$  denoted the activities of protein of composition corresponding respectively to the crystalline (less hydrated) and the dissolved (more hydrated) form, and  $a_{H_2O}$  the activity of the water),  $a_p$  was, for the saturated solution, strictly constant.

If now the solution were in so far ideal that  $a_{p, \times H_2O}$  were proportional to  $c_{p, \times H_2O}$ , it would evidently be found that the decrease in solubility could be calculated from the decrease in water vapour-pressure by means of the exponent  $X$  taken from Sørensen's analytical results. On account of the high molecular weight of the protein,  $X$  became very great and it had in fact been possible to account roughly for the salting out effect of ammonium sulphate on egg-albumen in this way.

On the other hand Sørensen's osmotic measurements showed that the assumption

$$a_{p, \times H_2O} \propto c_{p, \times H_2O}$$

is not strictly true, and for this reason the calculations mentioned above which he (Dr. Christiansen) carried out some years ago had not been published. If, however, Sørensen's hydration values were taken for granted an effect of this kind must exist even if the above method of calculation gave only a rough approximation, and similar effects must exist in certain other cases. See for instance Bjerrum's work<sup>8</sup> on the effect of the vapour pressure of water on  $H^+$ -activity as measured by means of the hydrogen-electrode.

Professor Sørensen had informed him that he was carrying on, with his collaborators, new experimental and theoretical work to investigate the special case of proteins more thoroughly.

**Professor Scatchard** (*communicated*) said that, as stated explicitly in an earlier discussion of the same subject,<sup>9</sup> he considered that the results he had cited showed, not that the effects must be attributed to electrical forces, but that they might be explained without demanding improbable changes of dielectric constants or ionic sizes. However, the arguments of Dr. Christiansen did not convince him that this explanation was erroneous. Sørensen's proof that the egg albumen is more highly hydrated in solution than in the crystalline state depended on the assumption that the activity coefficient of ammonium sulphate is independent of the albumen concentration. Yet albumen, if it is salted out, must increase the activity coefficient of the salt. The effect might be calculated from the equations given in his (Professor Scatchard's) paper and explained quantitatively the distribution of ammonium sulphate across the membrane without any change in the hydration of the albumin. Since this result might also be obtained thermodynamically, that is without any physical assumptions from the extrapolated solubility curve, this did not mean that the experimental results cited by Dr. Christiansen confirmed the electrical theory, but only that they could not disprove it. As far as the present experiments indicated, the salting out of albumen might be due to hydration, to electrical effects, or to a combination of the two.

As regards the hydrogen ion, the results given in his paper, as well as other evidence from varied sources, seemed to him conclusive proof that the hydration must be very much smaller than that computed by Professor Bjerrum, so that the increasing activity coefficients must be due to some

<sup>8</sup> *Z. anorg. Chem.*, **109**, p. 275, 1920.

<sup>9</sup> *Chem. Reviews*, **3**, 383 (1927).

other cause, possibly to a decrease in the dielectric constant as assumed by Hückel.

He wished to emphasise his opinion that the most important test of the theory lay in the results for solutions whose dielectric constants had been directly measured.

**Professor Brönsted** said that the answer to the question of the applicability of the laws of strong electrolytes to weak electrolytes was that the laws of the ions were fundamentally independent of their participation in chemical equilibria. The study of weak electrolytes therefore might be, and actually was, of considerable assistance in determining these laws.

The particular case of a concentrated solution of HCl, in which the acid seemed to be a weak electrolyte, presented itself as a good example of the complexity of concentrated solutions and the appearance of general medium effects to which he has called attention in his paper. The steep increase in HCl vapour pressure (or activity) in the range of concentrated HCl solutions was not explained by the increase in ionic association (in fact, the occurrence of any such equilibrium necessarily involved a diminution in the activity), but was determined by the particular solvent effect upon the activity coefficients of all molecules entering the equilibrium. Such very high solvent effects were well known from the behaviour of only partly miscible solvents.

**Professor Harned** said that since equation (1) in Professor Allmand's paper was purely empirical, he had never considered it more than a useful thermodynamic device. However, he believed that it had a greater range of validity than Professor Allmand concluded. In the first place, in Table II., he found that the calculated minimum occurred at the same concentration as the observed minimum in the case of KCl but not for NaCl or LiCl. This was due to the fact that at the higher concentrations the values of the activity coefficients used to evaluate the constants in Table I. were in error to a considerable extent. The values used were taken from Lewis and Randall.<sup>10</sup> He doubted whether the second minimum existed.<sup>11</sup> No evidence for this had been obtained from electromotive force or freezing-point data. The accurate work of Guntelberg<sup>12</sup> on hydrochloric acid revealed no such behaviour. Further, in the case of mixtures, the experimental validity of the linear term seemed to be confirmed.<sup>13</sup>

**Professor Lowry**, speaking in reference to the question of solvation, said that Mr. Fowler's picture of water being attracted to an ion *in virtue of its properties as a dipole* implied that the water would be oppositely oriented about a positive and a negative ion. This opposite molecular orientation of the atmosphere of solvent was suggested by Ciamician as long ago as 1891<sup>14</sup> and reappeared in a modified form in some of Dr. Ulich's formulæ. The most interesting feature of Dr. Ulich's paper, however, was the conclusion that the hydrogen ion carries a single molecule of water, since this corresponded precisely with the view that the acidic hydrogen of an aqueous acid is not present as a free proton, but as an oxonium ion  $\text{H}_2\text{O} + \text{HCl} \rightleftharpoons \text{OH}_3^+ + \text{Cl}^-$ .<sup>15</sup> The ions  $\text{Br}^-$ ,  $2\text{H}_2\text{O}$  and

<sup>10</sup> Lewis and Randall, "Thermodynamics."

<sup>11</sup> Harned, *J. Am. Chem. Soc.*, **44**, 252 (1922).

<sup>12</sup> Guntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

<sup>13</sup> Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

<sup>14</sup> *Z. Physik. Chem.*, **1891**, **6**, 403.

<sup>15</sup> Compare *Chemistry and Industry*, 1923, **42**, 1048.

Cl,  $3\text{H}_2\text{O}$ , might then be compared with 4- and 6-co-ordination compounds, with four and six atoms of *hydrogen* surrounding the negative radical, whereas, in order to form a 6-co-ordination compound of a kation it would be necessary to provide six atoms of *oxygen* as in  $\text{Na}^+, 6\text{H}_2\text{O}$ . The opposite orientation of the molecules might therefore account in part for the fact that kations tended to be more heavily hydrated than anions.

## INDEX.

*Figures in heavy type against authors' names indicate personal contributions to the discussion*

- ACTIVITY, 416, 467, 500, 504.  
 — in methyl alcohol, 491.  
 — of  $\text{MgSO}_4$ , 353.  
 — of  $\text{ZnCl}_2$ , 480.  
 — of H ion in mixed solvents, 516.  
 — coefficients, 417, 422, 463, 498, 507, 536.  
 — — calculation of, 502.  
 — — of aqueous solutions, 503, 505.  
 — — — strong acids in homoanionic salt solutions, 462.  
 — — — strong hydroxides in homocationic salt solutions, 464.  
 — — — concentration curves, 470, 478.  
 — — measurements, 353.  
 Adair, G. S., **536**.  
 Adams, 425, 426.  
 Albumen, hydration of, 539.  
 Allmand, A. J., **349, 413, 470, 477**.  
 Anomalies, 445.  
 Association, 344, 349, 356, 434.  
 Atmosphere, ionic, 334, 342.  
 $\alpha$ -values, 346.  
 BANCROFT, W. D., 499.  
 Bates, S. J. and Kirchman, H. D., 372.  
 Baxter and Wallace, 379.  
 Bell, R. P., **396**.  
 Bi-bivalent salts, 352.  
 Birchbock, 382, 383.  
 Bjerrum, N., 344, 358, 374, **376, 403, 416, 418, 429, 432, 445, 469**.  
 Boiling-point raising, 503.  
 Born, 367, 391.  
 Boundary potential, 539.  
 Bousfield, 350, 477.  
 Bragg, 396.  
 Bray and Hunt, 344.  
 Bredig and Shirado, 372.  
 Bromide sodium, solubility of, in the presence of sodium nitrate, 489.  
 Brönsted, **375, 416, 431, 434, 469, 470, 541**.  
 Brownian movement, 336, 338, 342.  
 Buckley, P. S., **491**.  
 Bury, 504.  
 Busch, 397, 413.  
 Butler, J. A. V., **538**.  
 CATAPHOROSIS, 396.  
 Chapman, D. L., **443**.  
 Charge, ionic, 396.  
 Christiansen, A., **539**.  
 Cohn, 429.  
 Complex, hydrogen ion, 539.  
 Compound, alcohol-water, 518, 521.  
 Concentration, activity ratio, 417.  
 — vapour pressure curves, 477.  
 Conductivity, 334, 341, 415.  
 — of HCl and NaCl, 344.  
 — —  $\text{MgSO}_4$ , 348.  
 Contact, ionic, direct, 365.  
 Contraction on solution, 450.  
 Cowperthwaite, I. A., **400**.  
 DAVIES, **351, 433**.  
 Debye, P., **334, 341, 378, 391**.  
 Debye and Pauling, 424.  
 Demassieux, 470.  
 Denison and Steele, 401.  
 Determination, conductivity and viscosity, 527.  
 Dew-point lowering, 504.  
 Dielectric constants, 461.

- Dielectric constants, variation in, 456.  
 — polarised, theory of, 538.  
 Diffusion, 350, 356.  
 Dilution, heat of, 445, 450, 454.  
 — measurements of heats of, 538.  
 Dissociation, complete, 400, 402, 431, 443, 454, 500.  
 — , incomplete, 373.  
 — of uni-univalent salts, 354.  
 Distance, lattice, 358, 367, 379, 380.  
 Distribution, laws, molecular, 435.  
 — ratios, 506.  
 Douglas, 452.  
 Drude and Nernst, 450.
- EBERT, 370, 431.  
 Electrodes, Amalgam, 491.  
 Electrolyte, uni-univalent, 443.  
 — strong, ionisation of, 400.  
 Electrolytes, weak, 427, 508, 541.  
 Electro-osmosis, 383.  
 Electrophoresis, 338, 341.  
*E.M.F.* drift, 494.  
 Equation, Lorentz's, 377.  
 — Ostwald dilution, 404.  
 Equilibrium constant, 506.  
 — indicator-buffer, 428.
- FAJANS, K., 357, 375, 376, 408, 538.  
 Fajans, K., and, Jooß, 359, 360, 378, 361, 409.  
 Ferguson, A., 404, 414.  
 Fowler, R. H., 411, 424, 434.  
 Foxton, F. and Shutt, W. J., 480.  
 Frazer and Hartley, 348, 389, 394.  
 Freezing-point lowering, 406, 459, 503.  
 — measurements, 353.  
 Friction constant, 338.
- GHOSH, 422.  
 Gibbs', phase integral, of, 434.  
 Goldschmidt, 379, 539.  
 Goldschmidt, H., 380.  
 Gorke, 413.  
 Grimm, 361, 409.  
 Gross and Halpern, 425.  
 Guntelberg, 419, 421, 424, 430, 541.
- $H_2Cl$ , 369, 375.  
 $HCl_{ind.}$ , 368, 370.  
 $H_2O$ , 368, 370, 458.  
 $H_2O \cdot Cl$ , 368, 370, 376.  
 Hantzsch, 409, 432, 511.  
 Hardman and Lapworth, 389.  
 Harned, H. S., 374, 422, 429, 430, 431, 462, 541.  
 Harned and Fleysner, 389.  
 Hartley, H., 393, 396, 408.  
 Heckmann, 379.  
 Helmholtz double layer, 338.  
 Henderson, 467.  
 Herzfeld and Wolf, 409.  
 Hevesey, G., 376, 386.  
 Heydweiler, A., 359, 370.  
 Höjendahl, 450.  
 Holstamm, 374.  
 Huang, T., 401.  
 Hüchel, E., 333, 341, 358, 430.  
 Hund, 380, 411.
- Hüttig, 370.  
 Hydration, 356, 385, 464.  
 Hydrolysis, 513.
- INTERACTION, specific, 420.  
 Iodide—thiocyanate mixtures, viscosities and specific conductivities of, 530.  
 Ion, conductance of the ammonium, 402.  
 — — — chloride, 401.  
 — — — hydrogen, 402.  
 — — — nitrate, 403.  
 — hydrogen, 539.  
 — — hydrated, 520.  
 — — in alcohol water mixtures, 516.  
 — transport number of the sodium, 497.  
 Ionisation, complete, 508.  
 — of, salts fused, 511.  
 Ions, associated, 433.  
 — complex, 357.  
 — negative, heat capacity of, 450.  
 Isodynes, 474.
- KENDALL and Sloan, 470.  
 King, F. E., 522.  
 Kohbrausch, 340, 381, 397.  
 Kraus, C. A., 488.  
 Kukenthal, 370.
- LAMER, 420, 430.  
 Lannung, 447.  
 Lapworth, 539.  
 Lattey, R. T., 412.  
 Lewis, G. N., 417, 499.  
 Lewis and Linhart, 418.  
 Linhar, G. A., 372.  
 Lorenz, R., 358, 377, 392, 404, 481.  
 Lovelace and Frazer, 477.  
 Lovelace, Frazer and Sease, 474.  
 Lowry, T. M., 508, 541.  
 Lucasse, 486.
- MACINNES, D. A., 400, 468.  
 Macinnes and Smith, 401.  
 McBain, J. W., 481.  
 McChlery, 394.  
 Micelle, ionic, 481, 510.  
 Millet, H., 515, 539.  
 Milner, 416, 422, 435.  
 Mobility, 335, 343, 351, 381, 384, 396.  
 — in non aqueous solvents, 388.  
 — — methyl alcohol, 393.  
 — ratios, 382.  
 Molecules, undissociated, 357.  
 Mueller, 403.
- NaCNS. molecular conductivities of, in alcohol, 530.  
 Natanson, 377.  
 Niggli, 362.  
 Non-electrolytes, 504, 539.  
 Nonhebel and Hartley, 389, 394.  
 Noyes and Baxter, 431.
- ÖHOLM, 350.  
 Onsager, 338, 341, 356.  
 Osmotic coefficient, 417.
- PARTINGTON, J. R., 522.  
 Partition coefficients, 447, 449.

- Pearce and Snow, 472, 474, 477.  
 Philbrick, 394.  
 Phillips, P., 377, 378.  
 Plotnikow, 511.  
 Polarisation, 357, 379, 498.  
 Polymerisation, 458.  
 Porter, A. W., 377, 413, 538.  
 Pressure, osmotic, 503.  
 Pring, J. N., 539.  
 Protein ion, activity coefficient of, 536.
- RADIUS, ionic, 344, 392, 426, 430, 445, 460.  
 Raikes, H. R., 393.  
 Randall, M., 498, 502.  
 — and Failey, 501.  
 Rawlins, F. I. G., 378.  
 Redlich, 340.  
 Refractivity, 357, 363, 365.  
 — changes, 358.  
 — in solution and in crystals, 366.  
 Reinkober, 379, 380.  
 Reis, 367.  
 Remy, H., 381, 414, 415.  
 Richards and Rowe, 445.  
 Ross, 394.  
 Ross Kane, N. L., 491.
- SALTS, uni-univalent, 397.  
 Scatchard, 418, 422, 430, 454, 538, 540.  
 Schmick, 390, 395.  
 Schreiner, E., 364, 370, 428, 431.  
 Setschenow, 458.  
 Seward, R. P., 488.  
 Sodium chloride, solubility of, in isopropyl alcohol at 25° in the presence of ammonium nitrate, 489.  
 Solubility, determinations, 488, 522.  
 — of salt in a mixture of electrolytes, 506.  
 — salt; of one, in presence of another, 491, 525.
- Solutions, concentrated salt, 429.  
 — mixed, 454.  
 Solvation, 391.  
 Sørensen, 539.  
 Soret effect, 448, 450, 538.  
 Spangenberg, 360.  
 Stokes' law, 338, 340, 350, 391, 395.  
 Strength, ionic, 419, 432.  
 Sutherland, 350.  
 System  $\text{KCl}-\text{PbCl}_2-\text{H}_2\text{O}$ , 470.
- TAMMANN, 374.  
 Tanner, C. C., 538.  
 Tetra-ethylammonium iodide, 389, 512.  
 Theory, statistical, 434.  
 Transport, numbers, 381, 385, 387, 398, 414, 486.
- ULICH, H., 388, 397, 414.  
 Uni-univalent salts, 358.
- VAN VLECK, 379.  
 Vapour pressure lowering, 503.  
 — — measurements, 371, 472, 474, 484, 506.  
 Viscosity, 349, 356.  
 Vogel, I., 404, 414.
- WALDEN, 388, 392, 397, 404, 481, 510.  
 Wasastjerna, 360, 396.  
 Washburn, 350.  
 Water a dipole, 541.  
 — the activity of, 503.  
 Water sheaths, 381, 385, 387.  
 Widman, 362.  
 Wolfenden, J. H., 491.  
 Wright, C. P., 491.  
 Wynne-Jones, W. F. K., 413, 433.
- ZWICKY, 438.

# THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR.

BY L. W. ELDER, JR., AND E. K. RIDEAL.

(Received 23rd April, 1927.)

While the decomposition of hydrogen peroxide has been extensively studied in water solution, only one published report of its behaviour in the vapour phase has come to our attention.<sup>1</sup> Hinshelwood finds the reaction to proceed as a unimolecular surface reaction on glass at 76° C. The elimination of the difficulties due to diffusion which arise in the study of, *e.g.*, platinum catalysis in aqueous solutions, suggested the possibility of clearing up the kinetics of this and similar  $H_2O_2$  catalyses by working in the vapour phase. While this original programme has not been completed, the authors feel that the results so far achieved have sufficient interest to warrant their presentation in this paper.

## Apparatus and Method.

The reaction vessel A (Fig. 1) was a transparent Vitreosil bulb of 300 c.c. capacity provided with a side tube and ground-in stopper for charging, and a fine capillary outlet.

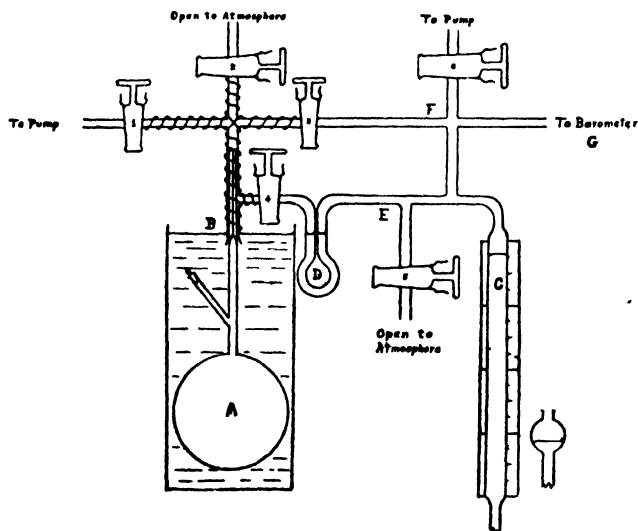


Figure 1

thin rubber gasket lubricated with glycerine and fitting snugly into the conical end of tube B. The latter, together with the connecting tubes enclosed within the vacuum taps 1, 2, 3, and 4, was kept at a temperature of 120° C.

<sup>1</sup> Hinshelwood and Prichard, *J. Chem. Soc.*, 123, 2726, 1923.

by means of a wound-on resistance coil in series with a lamp-bank. A minute amount of  $\text{H}_2\text{O}_2$  diffusing through the capillary into this area is rapidly decomposed and provides a pocket of  $\text{O}_2$  and  $\text{H}_2\text{O}$  vapour which diminishes further diffusion of  $\text{H}_2\text{O}_2$  to negligible proportions. The pressure change was measured at constant volume by balancing a fixed amount of air in the connecting tubes E, F, by means of a column of mercury C against the bulb pressure through a liquid paraffin guage D which was levelled before each reading. Since the elevation of the mercury column C for any given pressure change in A depends on the amount of air in the right half of the apparatus, an open-end barometer column G is provided for use in calibrating the readings at C. This apparatus avoids the undesirable diffusion of Hg vapour into the reaction vessel and also provides a more sensitive manometric system than is available in a direct-reading mercury manometer. It is thus possible to read directly to the equivalent of 0.1 mm. Hg without a telescope and the gauge is sensitive to about 0.02 mm. Hg. A sliding platform equipped with pulley and counterpoise provides for raising and lowering a small thermostat in which the reaction vessel is immersed during an experiment.

$\text{H}_2\text{O}_2$  was prepared from two different sources. One lot was distilled from a mixture of the urea— $\text{H}_2\text{O}_2$  crystals marketed under the trade name of "Hyperol," and phosphoric acid; 50 g. of "Hyperol" and 35 g. of an approximately 90 per cent.  $\text{H}_3\text{PO}_4$  distilled under a pressure of 38 mm. between the temperatures of  $55^\circ$ – $62^\circ$  yield a product which is nearly 60 per cent.  $\text{H}_2\text{O}_2$ . The concentration of the  $\text{H}_3\text{PO}_4$  must be controlled fairly closely, as an acid which is too dry only promotes intramolecular decomposition, most often of an explosive nature. When the temperature of the mixture is kept below  $85^\circ$ , the distillation proceeds quite smoothly. The distillate was found to be free from phosphate.

The second lot was prepared according to the method of Kilpatrick and Rice<sup>2</sup> and concentrated to approximately 60 per cent.

No difference in behaviour could be detected between these two preparations.

From the data of Maas and Hiebert<sup>3</sup> on the vapour pressure of  $\text{H}_2\text{O}_2$ , it was found that the maximum weight of  $\text{H}_2\text{O}_2$  to be used in the bulb without saturation is 22 mg. at  $80^\circ$ . A capillary pipette was constructed to deliver 0.020 c.c. of the 60 per cent. solution. The material was introduced through the side tube and the apparatus pumped out at room temperature by a "Hyvac" oil pump. With all taps closed, the thermostat was then put in place and the initial readings of pressure and time taken after an interval of about 2 min., by opening tap 4 and adjusting the paraffin levels by means of the mercury column in C. At the end of a run the bulb was heated to about  $300^\circ$ – $400^\circ$  in a Bunsen flame, the thermostat replaced, and an "infinity" reading taken, corresponding to complete decomposition of the  $\text{H}_2\text{O}_2$ .

### Composition of the Vapour.

Since the composition of the  $\text{H}_2\text{O}_2$  preparation used (approx. 60 per cent.) corresponds to a monohydrate, it was of interest to investigate the composition of the vapour below its saturation pressure, as the existence of a hydration equilibrium in the vapour might seriously affect the significance of the pressure changes during decomposition.

<sup>2</sup> *J. Amer. Chem. Soc.*, **48**, 3019, 1926.

<sup>3</sup> *Ibid.*, **46**, 2693, 1924.

A measure of the complexity of the vapour is furnished by a comparison of the vapour pressure of the original mixture before decomposition with that of the resulting water vapour, which one assumes to be composed of single molecules.<sup>4</sup>

To do this it was necessary to measure the pressure of water vapour, apart from the oxygen pressure, at the end of the decomposition. This was achieved by freezing out the water by means of an ice bath surrounding the bulb and measuring the  $O_2$  pressure at  $0^\circ$ . Converting the latter to the temperature of the thermostat and subtracting from the final total pressure yields the desired water vapour pressure.

Barometer Readings.	No. 58. At $85^\circ$ .	No. 67. At $95^\circ$ .
Dry and pumped out . . .	$785.5 - 29.5 = 756.0$	$755.0 - 11.1 = 743.9$
$H_2O_2$ added . . .	$744.0 - 74.0 = 670.0$	$714.5 - 55.0 = 659.5$
"Infinity" . . .	$736.0 - 82.5 = 653.5$	$708.0 - 62.5 = 645.5$
"Infinity" at $0^\circ$ . . .	$777.0 - 44.0 = 733.0$	$742.5 - 24.5 = 718.0$
	<hr/> 756.0	<hr/> 743.9
	<hr/> 733.0	<hr/> 718.0
Mm. $O_2$ + sat'd $H_2O$ . . .	<hr/> 23.0	<hr/> 25.9
V.P. of ice . . .	<hr/> 4.6	<hr/> 4.6
Mm. $O_2$ at $0^\circ$ . . .	<hr/> 18.4	<hr/> 21.3
$18.4 \times 358/273 = 24.2$ mm. $O_2$ at $85^\circ$		$21.3 \times 368/273 = 28.7$ mm. $O_2$ at $95^\circ$
	<hr/> 756.0	<hr/> 743.9
	<hr/> 653.5	<hr/> 645.5
Mm. $H_2O + O_2$ . . .	<hr/> 102.5	<hr/> 98.4
Mm. $O_2$ . . .	<hr/> 24.2	<hr/> 28.7
Mm. $H_2O$ at end of reaction . . .	<hr/> 78.3	<hr/> 69.7
	<hr/> 756.0	<hr/> 743.9
	<hr/> 670.0	<hr/> 659.5
Mm. $H_2O, H_2O_2$ mixture at beginning	<hr/> 86.0	<hr/> 84.4

Since the total vapour pressure of water at the end of the reaction is no greater than that of the mixture at the beginning, it is clear that the original unsaturated vapour consists of simple molecules, one  $H_2O_2$  for every new  $H_2O$  present in the final vapour.

### Glass and Quartz.

Preliminary attempts to measure the decomposition rate in glass bulbs produced no significant results, owing to a lack of reproducibility, irrespective of the pre-treatment of the glass. Some indication was obtained, however, that the reaction, at least in its early stages, is, contrary to Hinshelwood, a zero order reaction passing into some form of unimolecular or inhibited zero order reaction in the final stages. Further work on this point is planned for the near future.

Quartz was found to yield more or less reproducible results when cleaned with chromic acid cleaning mixture, heated almost to boiling, rinsed thoroughly with conductivity water and baked out just below a red heat with a Bunsen flame. The curve (Fig. 2) illustrates the type of reaction which occurs at  $85^\circ$ . The significant thing about these reactions on quartz is that only a relatively small portion of the  $H_2O_2$  has decomposed when the

<sup>4</sup> Richards and Chadwell, *J. Amer. Chem. Soc.*, **47**, 2283 (1925).

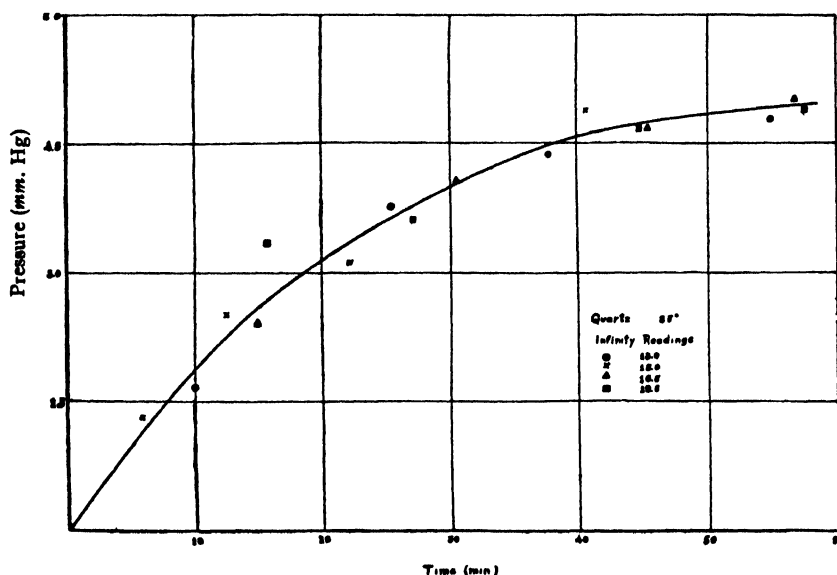


FIG. 2.

reaction comes to an abrupt end. This is shown most convincingly by the following data taken at 95°:—

No. 76.		No. 78.	
$t$ (min.).	$p$ (mm. manometer).	$t$ .	$p$ .
7	5.0	14	6.5
16	6.5	27	6.5
30	10.0	40	11.5
46	10.0	50	11.5
60	10.0	58	11.5
70	10.0		
Infinity	77.0	Infinity	74.0

The conclusion to be drawn is that we are dealing with a reaction which is strongly inhibited by the reaction products. This conclusion is verified by the application of the equations derived from the assumption that the inhibitor may be molecular or atomic oxygen. The following equations are applied to four runs:—

Unimolecular,— 
$$K_1 = \frac{1}{t} \log \frac{a}{a-x}.$$

Unimolecular with inhibition by  $O_2$ ,— 
$$K_2 = \frac{1}{t} \left( a \log \frac{a}{a-x} - x \right).$$

Zero with inhibition by  $O_2$ ,— 
$$K_3 = \frac{1}{2t} x^2.$$

Zero with inhibition by  $\sqrt{O_2}$ ,— 
$$K_4 = \frac{2}{3t} x^{3/2}.$$

No.	<i>t.</i>	<i>x.</i>	$K_1$	$K_2$	$K_3$	$K_4$
55	6	6.0	0.00663	- 0.547	3.00	1.63
	12	10.5	0.00570	- 0.462	4.59	1.89
	22	14.0	0.00451	- 0.327	4.46	1.58
	41	22.5	0.00422	- 0.261	6.17	1.74
54	10	10.0	—	—	5.00	2.11
	26	23.0	—	—	10.2	2.83
	38	26.5	—	—	9.21	2.39
	55	29.0	—	—	7.64	1.89
62	15	10.5	—	—	3.67	1.51
	31	18.0	—	—	5.22	1.64
	46	20.0	—	—	4.35	1.30
	57	22.0	—	—	4.25	1.21
65	16	15.0	—	—	7.04	2.42
	27	16.5	—	—	5.00	1.65
	45	21.0	—	—	4.89	1.42
	58	21.5	—	—	3.98	1.15

While these figures show that the reaction is unquestionably zero order with some sort of inhibition, it is hardly possible to decide whether the inhibitor is  $O_2$  or  $\sqrt{O_2}$ ; but the results of the following experiment at  $95^\circ$ , in which the remaining  $H_2O_2$  was frozen out and the reaction products pumped off after the initial decomposition had stopped, show that the freshly desorbed surface again decomposes an approximately equivalent amount of  $H_2O_2$  and again comes to a stop long before the complete disappearance of the  $H_2O_2$ .

No.	<i>t.</i>	<i>p.</i>	<i>t.</i>	<i>p.</i>
79	10	0.5	5	2.0
	25	7.5	14	4.0
	35	5.0	26	14.0
	48	6.5	33	14.0
Pumped out in ice bath for 8 minutes.			Infinity	54.0

It is hardly conceivable that atomic oxygen could exist on a surface so weakly adsorptive as to be desorbed in a few minutes by evacuation at  $0^\circ$ , hence we are forced to conclude that it is molecular  $O_2$  which is responsible for the inhibition.

### Platinum.

Once more with platinum we are faced with considerable difficulty in preparing a reproducible active surface. A length of Pt wire 0.225 mm. in diameter, having a total surface of 38.0 mm.<sup>2</sup> was cleaned in hot chromic acid, rinsed in conductivity water and dried in the quartz bulb at  $300^\circ$  before each run. As shown below, the decomposition at  $80^\circ$  was strictly unimolecular, but duplicate runs gave widely varying values of  $K_1$ . Corrections for the very slow decomposition on the quartz which must be involved in the measured results made a difference smaller than the mean variation among the uncorrected results.

## 550 DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR

54.0 mm. is the final pressure reading when reaction has ceased. If  $a$  is set equal to the infinity value, which is 66.0 mm., the lower set of figures is obtained—

No. 103.

$a$ .	$t$ .	$x$ .	$a - x$ .	$\text{Log } \frac{a}{a - x}$ .	$K_1$ .	$K_2$ .
54.0 mm.	3	14.5	39.5	0.1358	0.0453	—
	11	35.0	19.0	0.4536	0.0412	—
	18	44.5	9.5	0.7547	0.0418	—
	26	51.0	3.0	1.2553	0.0483	—
	35	53.0	1.0	1.7324	0.0495	—
					Av. = 0.0454	
66.0 mm.	3	14.5	51.5	0.1077	0.0359	— 2.47
	11	35.0	31.0	0.3281	0.0299	— 1.22
	18	44.5	21.5	0.4871	0.0271	— 0.683
	26	51.0	15.0	0.6434	0.0247	— 0.330
	35	53.0	13.0	0.7056	0.0202	— 0.183
	41	54.0	12.0	0.7403	0.0181	— 0.124

It will be observed that the infinity reading is high as compared with an asymptotic value and, further, that the reaction appears to give unimolecular constants only when the final pressure reading is taken as the measure of  $a$ . The difference, amounting to  $(66.0 - 54.0) \times 11.0/66.0 = 2.0$  mm., undoubtedly corresponds to  $O_2$  adsorbed on or dissolved in the platinum, which reappears when the apparatus is baked out. This hypothesis is in agreement with the view that the rate of decomposition is in reality a rate of diffusion through a film of adsorbed  $O_2$ .<sup>5</sup>

The failure of the equation relating  $t$  and  $p$  for a unimolecular reaction inhibited by  $O_2(K_2)$  shows that the adsorbed  $O_2$  does not enter into the kinetics of the reaction.

### Mercury.

It seemed to be of particular interest to investigate the behaviour of  $H_2O_2$  vapour on mercury in view of its well-known periodic reaction in aqueous solution.<sup>6</sup>

There is a well-defined induction period to be observed in nearly every case, followed by a fairly rapid reaction running to completion in about 20 minutes. When further pressure change had ceased, the bulb was pumped out at the temperature of the thermostat and the remaining oxides of Hg decomposed by heating in a Bunsen until the residue had completely distilled to the upper portions of the bulb as metallic Hg.<sup>7</sup>

The pressure of the  $O_2$  released was measured and compared with that evolved during the reaction as follows:—

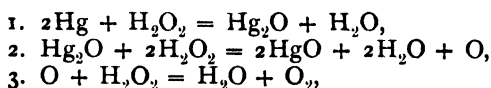
<sup>5</sup> Nernst, *Z. Elekt.*, **11**, 710, 1905; G. Lemoine, *Compt. rend.*, **162**, 657, 1916; Spitalsky and Kagan, *Ber.*, **59B**, 2900, 1926.

<sup>6</sup> Bredig and Weinmayr, *Z. physik. Chem.*, **42**, 601, 1903; G. Lemoine, *Compt. rend.*, **162**, 583, 1916.

<sup>7</sup> Taylor and Hulett, *J. physical Chem.*, **17**, 565, 1913.

No.	Hg Grams.	<i>t.</i>	<i>p.</i>	O <sub>2</sub> Evolved During Reaction.	O <sub>2</sub> from Oxides of Hg.
129	0.069	4	4.0	8.5 mm.	8.0 mm.
		9	8.0	—	—
		15	17.0	—	—
		21	36.0	—	—
		27	42.5	—	—
		30	42.5	—	—
134	0.120	5	15.5	6.0 mm.	6.0 mm.
		10	26.0	—	—
		16	29.0	—	—
		22	30.5	—	—
		25	30.5	—	—

These figures indicate that the decomposition of H<sub>2</sub>O<sub>2</sub> on Hg is coupled rather than catalytic. The decomposition of one molecule of H<sub>2</sub>O<sub>2</sub> is induced by the oxidation of one Hg<sub>2</sub>O to HgO. The initial induction period represents the initial oxidation of Hg to Hg<sub>2</sub>O, a reaction involving no pressure change. A mechanism of the following sort may be postulated—



in which reactions 1 and 2 are the slow reactions.

It is interesting to note that neither oxide is reduced by H<sub>2</sub>O<sub>2</sub> vapour, hence the reaction, unlike that in aqueous solution, is not periodic. This fact is further exemplified by the following series of experiments, in which the same sample (0.0605 g.) of Hg was exposed to three successive charges of H<sub>2</sub>O<sub>2</sub> at 80°. During the third run the Hg surface was completely oxidised to yellow HgO, when the reaction stopped after about 20 per cent. decomposition.

No. 121.		No. 122.		No. 123.	
		Hg from No. 121 Coated with Black Oxide.		Hg from No. 122, Black Streaked with Yellow.	
<i>t.</i>	<i>p.</i>	<i>t.</i>	<i>p.</i>	<i>t.</i>	<i>p.</i>
11	40.0	2	18.0	2	6.5
15	44.0	4	23.0	6	6.5
18	44.0	8	28.5	—	—
		10	28.5	—	—
Pumped out at 80°		Pumped out at 80°			

### Summary.

1. An apparatus is described for the measurement of the rate of decomposition of H<sub>2</sub>O<sub>2</sub> vapour in constant volume.
2. A method is described for preparing pure concentrated H<sub>2</sub>O<sub>2</sub> from the urea-H<sub>2</sub>O<sub>2</sub> crystalline compound known as "Hyperol."
3. The vapour under about 85 mm. pressure at 85° C. is shown to be composed of simple molecules, free from any measurable hydrate.

4. The thermal decomposition on quartz at  $85^\circ$  is a zero order reaction inhibited by  $O_2$ , which stops about 80 per cent. short of completion.

5. On Pt wire,  $H_2O_2$  vapour undergoes an apparently unimolecular decomposition which is shown to be very probably determined by the rate of diffusion through an adsorbed or dissolved layer of  $O_2$ .

6. The reaction on a mercury surface consists of a preliminary direct oxidation of Hg to  $Hg_2O$ , followed by coupled oxidation of  $Hg_2O$  to  $HgO$ , in which an amount of oxygen is liberated proportional to the amount of  $HgO$  formed. It is shown that  $HgO$  is not reduced by  $H_2O_2$  vapour.

The authors take pleasure in acknowledging assistance from the Frederick Sheldon Fund of Harvard University, U.S.A., which has made it possible for the junior author to undertake this work.

## THE CRITICAL POTENTIALS OF NITROGEN AND THE NATURE OF ACTIVE NITROGEN.

By A. S. LEVESLEY.

*Communicated by* DR. W. E. GARNER.

(Received 7th June, 1927.)

The energy levels of the nitrogen molecule have not yet been satisfactorily elucidated, in spite of a large number of investigations on the resonance potentials of nitrogen and on the spectra emitted by nitrogen when subjected to electronic bombardment. The diversity of the results on resonance potentials shows that the first excitation potential of the nitrogen molecule is not yet determined with a sufficient degree of accuracy, and that more experimental work is needed on the subject. The case of nitrogen is particularly interesting since a knowledge of the energy levels of the molecule will throw some light on the nature of "active nitrogen" discovered by Professor Lewis in 1900.

In a paper read before the American Physical Society<sup>1</sup> Birge gave a set of electronic energy levels for the nitrogen molecule based on an analysis of its band spectra. Birge was led to the conclusion that the second and fourth groups of bands of the neutral molecule have a common final state, and that this final state is the same as the initial state of the first positive group of bands. In assigning vibrational quantum numbers to the bands of these systems, Birge showed that the heads for the first, second, and fourth groups, corresponding with the quantum jumps  $O \rightarrow O$ , occur at  $\lambda = 9106$ ,  $\lambda = 3371$ , and  $\lambda = 2262$  respectively. According to the theory of band spectra these frequencies are determined solely by the change in the electronic energy of the molecule, and therefore we have, applying the Einstein relation, the values 1.4 volts, 3.6 volts, and 5.5 volts respectively for the electronic energy changes associated with the emission of each head.

Now it is known that there are no absorption bands of nitrogen in the portion of the spectrum corresponding to the wave-length regions of the bands under consideration. Nitrogen gas is transparent down to about  $\lambda = 1850$ ; thus it is improbable that the electron transitions associated

<sup>1</sup> *Physical Rev.*, 1924, **23**, 294.

with the emission of any of these band systems return the nitrogen molecule to its normal condition. Birge concluded therefore, that the final state of the first positive group does not represent the stable state of the molecule, but that there is a further energy level which corresponds to the stable state. The wave number associated with the change from the final state of the first positive group to the stable state was stated tentatively by Birge to be about 65,000 corresponding to 8.0 volts.

The experimental work on the excitation of nitrogen by electronic bombardment has given a range of values for the resonance potential, lying between 6.3 volts and 9.0 volts. (A summary of these values is given in Table I.). This experimental evidence is not in very satisfactory agreement with Birge's scheme of energy levels, and with a view to the elucidation of some of the considerations mentioned above, the present investigation was undertaken. The lowest excitation potential of nitrogen has been determined by the method devised by Hertz:<sup>2</sup> an experimental method which has not previously been used for nitrogen.

TABLE I.

Smyth . . . . .	<i>Physical Rev.</i> , 14, 409, 1919 . . . . .	$\left\{ \begin{array}{l} 6.29 \pm 0.06 \\ 7.3 \\ 8.29 \pm 0.04 \end{array} \right.$
Goucher . . . . .	<i>Physical Rev.</i> , 8, 561, 1916 . . . . .	7.4 $\pm 0.1$
Davis and Goucher . . . . .	<i>Physical Rev.</i> , 13, 1, 1919 . . . . .	7.5
Bishop . . . . .	<i>Physical Rev.</i> , 10, 244, 1917 . . . . .	7.5
Hughes and Dixon . . . . .	<i>Physical Rev.</i> , 10, 495, 1917 . . . . .	7.7
Bazzoni . . . . .	<i>J. Frank Inst.</i> , 57, 197, 1924 . . . . .	8.0
Foote and Mohler . . . . .	<i>Bur. Stan. Sci. Papers</i> , No. 400, 669, 1920 . . . . .	8.18 $\pm 0.1$
Smyth . . . . .	<i>Physical Rev.</i> , 14, 409, 1919 . . . . .	8.29 $\pm 0.04$
Boucher . . . . .	<i>Physical Rev.</i> , 19, 189, 1922 . . . . .	8.4 $\pm 0.1$
Brandt . . . . .	<i>Z. Physik</i> , 8, 32, 1921 . . . . .	8.5
Davis and Goucher . . . . .	<i>Physical Rev.</i> , 13, 1, 1919 . . . . .	9.0

### Experimental.

The design of the reaction vessel which is shown in Fig. 1 follows that

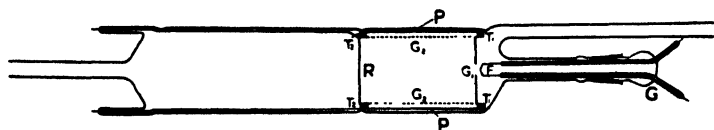


FIG. 1.

used by Hertz. The source of electrons is a short tungsten filament F, which was mounted on a ground glass stopper G in order to facilitate its removal for alterations or repairs. This stopper was used without any lubricant and when waxed on the outside, the point was perfectly gas-tight. The two cylinders P and R were made of copper. The inner cylinder R was 6.0 cms. long and 4.5 cms. in diameter: its walls were of copper gauze 1 mm. mesh. The outer cylinder P was 7.0 cms. long and 5.3 cms. in diameter. The distance between the filament and the cylinder R was made as small as possible—about 2 to 3 mms.—so that the electrons made few, if any collisions before entering the actual collision chamber. Before being assembled the metallic parts of the apparatus were thoroughly cleaned with nitric acid. This is essential to prevent the formation of contact potentials. The two cylinders were insulated by means of two glass rings T<sub>1</sub> and T<sub>2</sub>.

<sup>2</sup> *Z. Physik*, 1923, 18, 307.

The apparatus was evacuated by means of a mercury diffusion pump backed by a Töpler pump, and the pressure measured on a McLeod gauge sensitive to  $10^{-6}$  cms. Since the metallic parts of the apparatus were of copper, it was essential to exclude mercury vapour from the reaction vessel. With this end in view a trap immersed in liquid air, and a tube containing gold leaf were interposed between the pump system and the experimental tube.

The apparatus was baked out in an electric furnace at  $380^{\circ}$ - $400^{\circ}$  C. for several hours, and the electrodes bombarded by a stream of electrons from the filament. All the other parts of the glass apparatus which were not immersed in liquid air, were heated with a naked flame. It was found extremely difficult to get rid of the last traces of moisture. Finally the apparatus was washed out two or three times with nitrogen gas. Prior to each experiment the reaction vessel was baked out at  $380^{\circ}$ - $400^{\circ}$  C. for three hours.

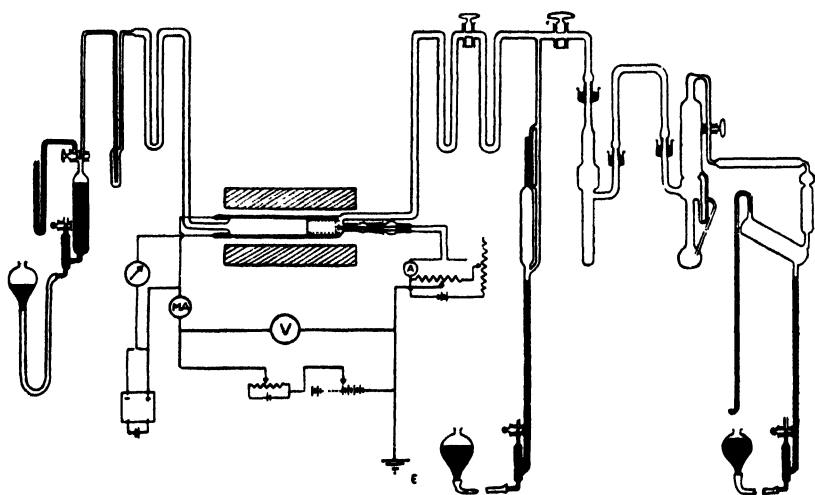


FIG. 2.

A diagram showing the general arrangement of the apparatus and the electrical connections is shown in Fig. 2. The centre of the filament was earthed by the method described by Richardson and Brown.<sup>3</sup> The accelerating voltage applied to the electrons was measured on an Elliot Standard voltmeter, and the current between the two cylinders R and P was measured on a Campbell Galvanometer. This instrument had a sensitivity of 5 mm. per  $10^{-9}$  amp. at a scale distance of 1 metre, and a resistance of 330 ohms. Its long period, 43 secs., helped to keep the readings steady. Great care had to be exercised on the insulation of the galvanometer circuit. For insulation light vacuum oil and freshly scraped ebonite were used throughout.

The nitrogen used in these experiments was prepared from ammonium sulphate and sodium nitrite. It was purified by bubbling through sulphuric acid and stored for at least twenty-four hours over an alkaline solution of ferrous sulphate. It was then dried by means of sulphuric acid and phosphorus pentoxide and finally passed over copper turnings heated to dull

<sup>3</sup>*Phil. Mag.*, 1908, 16, 360.

red heat. Before entering the reaction vessel itself, the gas passed through a trap immersed in liquid air.

For the experiments in which hydrogen was used, the commercial product was dried over phosphoric anhydride and purified by diffusion through a heated palladium tube.

### Results.

Typical results obtained from the measurements are shown in Fig. 3.

The curves marked I' show the current carried by the electrons across the annular space between the two cylinders R and P, plotted against the

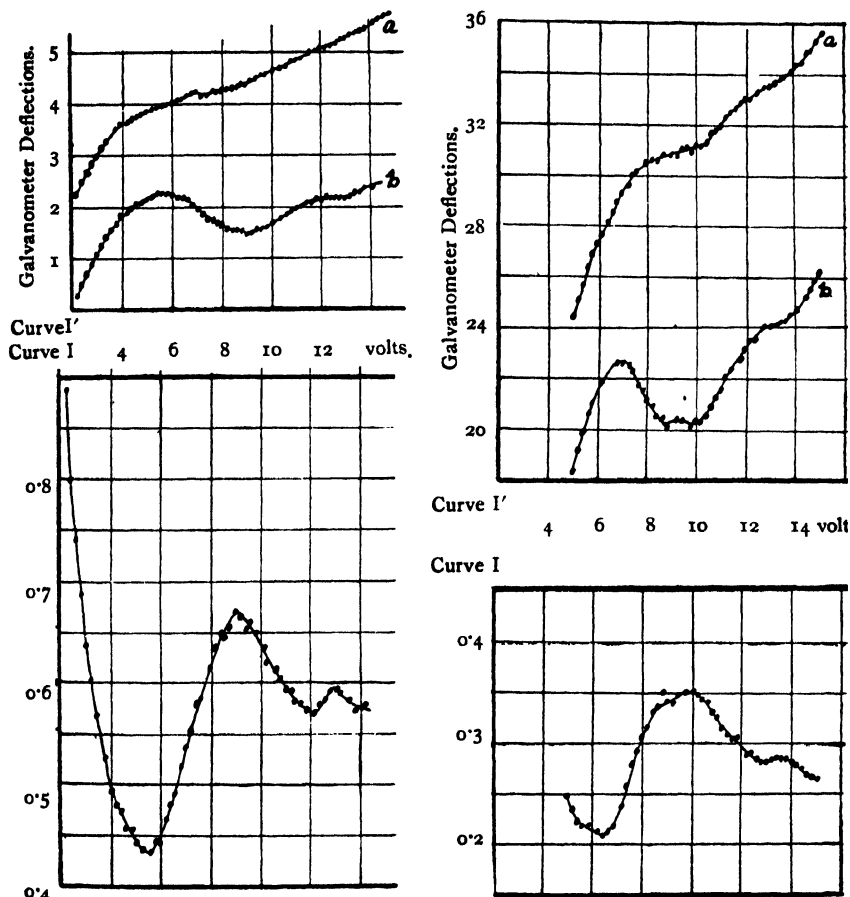


FIG. 3.

accelerating voltage applied to the electrons. I'a is the curve of the current when R and P are maintained at the same potential, and I'b is the curve of the current when the small auxiliary retarding field of 0.2 volt is maintained between the two cylinders. The curves marked I are obtained from I'a and I'b. The abscissæ represent the accelerating voltage applied to the electrons, and the ordinates a measure of the proportion of the current between R and P which is carried by very slow moving electrons. This is

obtained by dividing the difference between the two galvanometer deflections, for each voltage—with and without the auxiliary retarding field—by the total current between R and P when they are both at the same potential.

All the curves I show a broad maximum and a smaller subsidiary maximum. Starting at 5.0 volts or below, and increasing the accelerating voltage applied to the electrons in 0.2 steps, there is at first a continuous fall in the number of slow-moving electrons present in the gas. In the region of 6.4 volts this fall is suddenly arrested. The curves show a minimum value at this point, and on all the experimental curves obtained this minimum is the most well-defined feature. As the accelerating voltage is increased the number of slow-moving electrons increases rapidly up to about 8.5 volts, then the rate of increase becomes less rapid. The curves show a broad somewhat ill-defined maximum at about 9.5 volts. When the accelerating voltage is further increased the number of slow-moving electrons present decreases; the rate of decrease however is less than the previous rate of increase. The second maximum occurs between 12.5 and 13.0 volts.

The position of the first maximum of the curves I is given in Table II. for a series of 10 runs carried out at different pressures and with different filament temperatures.

TABLE II.

Run.	1.	2.	3*.	4*.	5*.	6.	7.	8.	9.	10.	Mean.	Probable Error.
Pressure (mm.)	0.04	0.04	0.05	0.06	0.07	0.10	0.10	0.04	0.09	0.09	—	—
1st Minimum	5.5	6.2	6.2	6.3	6.4	6.5	6.4	6.4	6.5	6.6	6.30	±0.02
2nd Minimum	12.0	13.3	—	—	—	12.9	12.8	12.4	12.9	12.9	12.60	—
Interval	6.5	6.1	—	—	—	6.4	6.4	6.0	6.4	6.3	6.30	±0.05

(Note: In the runs marked with an asterisk, *i.e.* runs, 3, 4, and 5, the readings were only taken as far as 9.0 volts.)

The second minimum, which is less well-defined than the first, occurs in the neighbourhood of 12.5 volts. Its position and its relation to the first minimum is also given in Table II. for the seven runs for which figures are available.

The figures make it appear probable that the second minimum is to be regarded as a multiple of the first minimum and caused by the impacting electrons having attained a velocity sufficient to enable them to make two inelastic collisions before having their velocity reduced to zero. It must be noted, however, that this double impact method of obtaining the true critical voltage is not so satisfactory in the case of multiatomic gases as in the case of the monatomic inert gases and the metallic vapours, chiefly owing to the difficulty of fixing the second point on the curve with a sufficient degree of accuracy.<sup>4</sup>

With regard to the first maximum of the curves I, this cannot be determined accurately, but in none of the runs considered in Table II. does it occur below 9.0 volts, and in none above 9.9 volts.

Some results obtained from experiments on mixtures of nitrogen and hydrogen are shown in Fig. 4.

<sup>4</sup> See Dymond, *Proc. Roy. Soc.*, 1925, A. 107, 291.

These curves are almost identical with the curves obtained for nitrogen alone. They show the same minimum at about 6.4 volts, and the broad maximum with the smaller subsidiary maximum. The results were difficult to obtain owing to the disappearance of the hydrogen under the "clean up" effect of the tungsten filament. In the experiment for which the results are shown, using a 50 per cent.  $N_2$  - 50 per cent.  $H_2$  gas mixture by volume, the initial pressure was 0.070 mm. and at the end of the run the pressure had fallen to 0.034 mm. The decrease in pressure was rapid at first and then became more gradual. Thus very low pressures of hydrogen were used and probably this explains why there are no evidences of critical potentials due to hydrogen on the curves obtained. A more satisfactory method would have been to have had the gas mixture streaming through the apparatus at constant pressure.

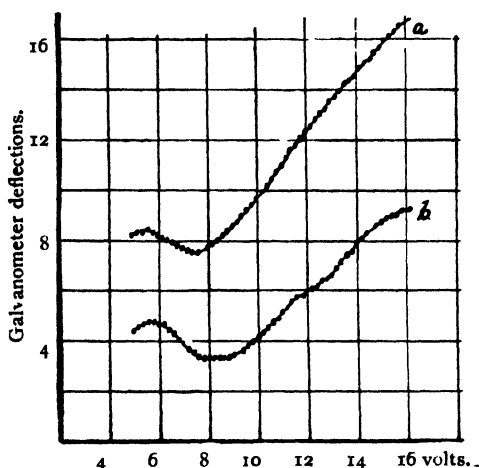
Incomplete as these results are, however, it seems possible to draw one conclusion from them. The fact that the minimum at 6.4 volts is just as pronounced as in the curves for nitrogen seems to prove that this low voltage effect is due to nitrogen and not to any nitric oxide contained in the gas as impurity.

According to Sponer<sup>5</sup> one would expect a critical potential due to nitric oxide in this region—at 5.4 volts to be exact, corresponding to the head of the  $O \rightarrow O$  band of the 3rd positive group ( $\lambda = 2269$ ), the stable state of the NO molecule being the final state of this group of bands.

Had nitric oxide been present in the experimental tube one would expect it to react, in the neighbourhood of the incandescent filament, with the hydrogen present, according to the equation,



By means of the Nernst Heat Theorem it is possible to calculate the value of the equilibrium constant  $K_p$  for the reaction at a temperature corresponding to that in the immediate neighbourhood of the filament. Using the approximate form of the theorem  $K_p$  is determined by the equation,



Curve I'

Curve I

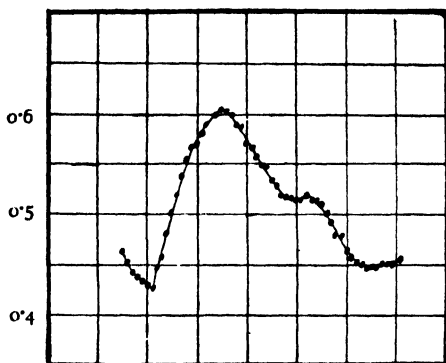


FIG. 4.

$$\log K_p = \frac{Q_p}{4.571 T} + \sum \nu 1.75 \log_{10} T + \sum \nu C_0$$

taking for  $T$  the value  $2173^\circ K$ , ( $1900^\circ C$ ).

then

$$\log K_p = 10.331$$

where

$$K_p = \frac{P_{H_2O}^2 \times P_{N_2}}{P_{H_2}^2 \times P_{NO}^2}$$

From this it is seen that the reaction goes practically to completion with the formation of nitrogen and water vapour. Thus one would expect, had the 6.3 volt effect been due to nitric oxide, a considerable modification in the curves on the addition of  $H_2$ . Since this is not obtained, it seems permissible to assume that the effect is due to  $N_2$ .

### Discussion of Results.

From the experiments which have been made it appears to be established that the collisions between nitrogen molecules and electrons become inelastic at the point when the latter attain 6.3 volts energy. Further the type of curve obtained seems to indicate that starting from this point the collisions are inelastic over a range of about 3.0 volts.

The last conclusion is not inevitable. The broad maximum obtained may be due to causes other than that of the collisions being inelastic over a range of energy values of the impacting electrons. A wide distribution of velocities in the electron stream would tend to make the maximum broad and rather ill defined. Again the shape of the curves may be occasioned to some extent by the metallic gauze used in the construction of the cylinder R. All the electrons which have made inelastic collisions with more than 0.2 volt surplus energy should theoretically not be stopped by the auxiliary retarding field. In practice, however, this gauze is not a perfect electrostatic shield, and the auxiliary retarding field must penetrate a short distance inside the "field free" space. This stray field would be sufficient to stop electrons of velocity greater than 0.2 volt from reaching the collecting electrode P if they approached it in an oblique direction.

The fact that the same results were obtained under different experimental conditions, *e.g.* with different filament temperatures and with filaments of different size, would seem to show that the two factors mentioned above were not entirely—even if in part—responsible for the breadth of curve obtained. Indeed from the diversity of energy changes which multiatomic molecules are capable of undergoing—as instanced by the emission of band spectra—one would expect *a priori* that the collisions between electrons and multiatomic molecules would be inelastic over a range of energy values of the impacting electrons.

Such a conclusion would help to explain the diversity of experimental values which have been obtained for the critical potentials of nitrogen. A fairly complete, but not exhaustive summary, of these values is given in Table I. It will be seen that all the values lie between 6.3 and 9.0 volts. Smyth measured three critical potentials in this region at 6.3, 7.3 and 8.3 volts; Davis and Goucher measured two at 7.5 and 9.0 volts respectively. Brandt obtained a whole series of critical potentials between 7.5 and 8.2 volts revealed as small kinks on the current potential curve. The value 6.3 volts found in the present investigation for the lowest point at which the collisions become inelastic agrees well with the value  $6.27 \pm 0.06$  volts

obtained by Smyth, though it should be mentioned that Smyth only obtained evidence of this critical potential at pressures lower than 0.026 mm.

As a test of Birge's theory, the experiments are inconclusive. On the basis of Birge's scheme of energy levels of the nitrogen molecule, one would expect a critical potential at 8.0 volts—the excitation potential of the head of the  $O \rightarrow O$  band of the system resulting from an electron transition between the final state of the first positive group and the stable state of the molecule. At the time when Birge's paper appeared such a band system for nitrogen had not been observed experimentally. Recently, however, such a band system has been observed by Sponer,<sup>6</sup> and although full details are not yet published, it is stated that the head of the  $O \rightarrow O$  band of the system does correspond to an excitation potential of 8.0 volts.

The inelastic collisions observed in the present investigation are very probably also associated with the excitation of another system of bands situated in the ultra violet region of the spectrum and having for the final state the normal state of the nitrogen molecule. The measurements, however, give little information concerning the position of the head of the null band of the system. The wave-length corresponding to the value 6.3 volts is  $\lambda = 1940$ , and that corresponding to 9.3 volts is  $\lambda = 1318$ . These values may be taken as giving some indication of the extent of the band system. To assume that the value 6.3 volts corresponds to the excitation of the head of the null band involves the further assumption that none of the energy gained by the nitrogen molecule, during an inelastic collision with a 6.3 volt electron, is used in increasing the vibrational or rotational energy of the molecule.

In conclusion it may be pointed out that no evidence has been obtained of a critical potential below 6.3 volts. This fact is interesting since Willey and Rideal,<sup>7</sup> from experiments on the heat developed during the action between "active nitrogen" and nitrous oxide, have obtained a value 42.5 Cals. (corresponding to 2.0 volts) for the energy of production of active nitrogen.

It is difficult to reconcile this low energy content of active nitrogen with the production of the after-glow bands (the energy associated with the emission being 11.5 volts according to Sponer<sup>8</sup>) and with the appearance of line spectra which are excited when active nitrogen is brought into contact with various elements, as for instance, iodine and mercury. Although it does not follow as a necessary conclusion, one might expect a critical potential of nitrogen at 2.0 volts if active nitrogen does in reality consist of metastable molecules carrying 2.0 volts surplus energy. Unfortunately the results obtained in the present investigation do not extend below 2.0 volts, and the above work had been concluded before the appearance of the paper by Willey and Rideal. There is no evidence of any such critical potential down to 2.0 volts.

### Summary.

The nature of the collisions between nitrogen molecules and electrons has been examined over a range of electronic energy values extending from 2.0 volts to 15.0 volts. It is shown that these collisions become inelastic at the point when the electrons attain 6.30 volts energy; further, starting from this point the collisions would appear to be inelastic over a range of about three volts.

<sup>6</sup> *Nature*, 1926, 118, 696.

<sup>7</sup> *J. Chem. Soc.*, 1926, 1804.

<sup>8</sup> *Z. Physik*, 1925, 34, 622.

The effect of the addition of hydrogen has been studied. This causes no modification in the results obtained, and it is concluded that the effect observed is due solely to nitrogen and not to any nitric oxide present in the gas as impurity. The inelastic collisions observed may be associated with the excitation of a band system of nitrogen, situated in the ultra violet region of the spectrum and having for its final state the stable state of the molecule.

The author wishes to express his thanks to Dr. W. E. Garner for his unfailing help and advice during the course of this investigation, and also to the Dept. of Scientific and Industrial Research for a Maintenance Grant.

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## THE VAPOUR PRESSURES OF DIPHENYL AND OF ANILINE.

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(Communicated by PROFESSOR R. WHYTLAW GRAY.)

*Received 10th June, 1927.*

In the course of comparing the vapour pressures of certain high-boiling-point organic substances with that of mercury by means of the Ramsay-Young rule, with a view to possible extrapolation to lower temperatures, an anomaly was observed in the case of diphenyl, using the data of Jacquerod and Wassmer.<sup>1</sup> The curve obtained by plotting  $T_1/T_2$  against  $T_1$  (where  $T_1$  and  $T_2$  are the absolute temperatures at which diphenyl and mercury respectively have the same vapour pressure) showed a sharp change of slope at about 224° C., the two arms being nearly straight lines. As the ratio  $T_1/T_2$  only changes by about 2 per cent. for 100° the graph can be made on a very large scale and is therefore very sensitive to small inaccuracies. A break such as is observed would therefore correspond to a discontinuity in the actual vapour pressure too small to be noticed on smoothing. As there appeared to be no other data for the temperature range considered a redetermination was undertaken.

Some measurements were also made on the vapour pressure of aniline at temperatures below 150° as the only published data for this range—those of Kahlbaum<sup>2</sup>—diverge widely from the Ramsay-Young extrapolation of the measurements at higher temperatures by Ramsay and Young themselves.<sup>3</sup>

### Experimental.

The apparatus was made on the principle of that described by Ramsay and Young,<sup>4</sup> but considerably modified in detail. The substance under investigation was placed in a bulb, containing a plug of glass wool, at the foot of a tube about 30 cm. long and 12 mm. in diameter. The top of the

<sup>1</sup> *Ber.*, **37**, 2533 (1904).

<sup>2</sup> *Ibid.*, **1**, 248 (1887).

<sup>3</sup> *Z. physikal. Chem.*, **26**, 603 (1889).

<sup>4</sup> *J. Chem. Soc.*, **47**, 42 (1885).

tube was connected through an upright condenser to a mercury manometer, and a side tube with a tap allowed the pressure within the apparatus to be altered as required. A short Anschütz thermometer, whose bulb was bound round with cotton wool, was hung inside the tube with its bulb about 10 cm. above the glass wool plug. The tube was heated by a bath of liquid whose surface was level with the thermometer bulb. The heating liquids used were sulphuric acid or molten paraffin wax, according to the temperature required. It was found that no precautions to regulate the pressure were needed. The liquid boiled in the glass wool plug and the vapour was condensed well above the top of the thermometer. The condensed liquid ran back through the upward stream of vapour on to the cotton wool surrounding the thermometer bulb, where the large surface ensured equilibrium. Once attained, the equilibrium remained undisturbed by slight fluctuations of the temperature of the bath.

Actually at each point the temperature of the bath was varied considerably, so that a number of readings of the vapour pressure at temperatures within a range of  $0.3$  or  $0.4^\circ$  could be obtained, and the mean taken. In this way although the thermometers could only be read with certainty to  $0.1^\circ$ , the actual error was probably much less, and most of the temperature readings are therefore given to the second decimal place. The thermometers were standardised by the National Physical Laboratory. The "closed" end of the manometer was kept evacuated by a mercury vapour pump, and the mercury levels read to  $0.01$  mm. by a cathetometer.

As a check on the method, measurements were made of the vapour pressure of water at various temperatures between  $30^\circ$  and  $100^\circ$ ; values in agreement with those given in the Tables of Landolt and Börnstein, were obtained.

### Results.

*Diphenyl.*—The diphenyl (Kahlbaum) was purified by repeated crystallisations from alcohol until a product of constant melting-point was obtained. The final melting-point was  $69.4^\circ$  C. (*cf.* Jacquerod and Wassiner,  $69.0^\circ$  C.). The experimental values are given in Table I. The points were plotted

TABLE I.  
DIPHENYL—EXPERIMENTAL POINTS.

T° C.	P (mm.).	T° C.	P (mm.).	T° C.	P (mm.).
153.31	37.25	197.55	173.27	232.04	439.59
157.78	45.15	199.59	185.97	234.95	473.79
159.30	49.43	200.12	188.52	235.40	480.71
159.60	49.70	202.83	199.93	236.97	497.74
160.20	50.37	203.93	207.20	241.90	564.32
162.57	55.90	206.50	225.86	243.65	589.98
163.13	56.72	206.73	227.15	246.90	638.46
166.60	63.58	210.25	251.06	247.20	643.36
170.22	72.29	211.85	261.33	248.45	666.34
176.14	86.40	214.07	278.30	249.35	680.26
180.78	101.94	218.23	310.34	250.80	705.17
186.00	123.79	221.60	338.80	251.30	712.48
187.55	126.51	224.14	362.81	252.42	726.07
189.28	136.48	228.17	402.69	253.69	749.62
191.71	145.31	231.15	433.31		

according to the Ramsay-Young method against mercury (Landolt-Börnstein) and the best curve drawn through them. Values were read off at even

## 562 VAPOUR PRESSURES OF DIPHENYL AND ANILINE

temperature intervals and converted back to vapour pressures. In view of the large scale, as pointed out above, this procedure may be considered very accurate: quite considerable errors in drawing the line or reading off the ratios would be inappreciable in the vapour pressure scale. These smoothed values are given in Table II.

TABLE II.  
DIPHENYL—SMOOTHED VALUES.

T° C.	P (mm.).	T° C.	P (mm.).	T° C.	P (mm.).
150°00	33°02	198°00	176°19	228°00	400°92
155°00	40°73	200°00	186°75	230°00	421°77
160°00	49°65	202°00	197°93	232°00	443°45
165°00	59°88	204°00	209°62	234°00	466°24
170°00	71°75	206°00	221°74	236°00	490°26
175°00	85°49	208°00	234°58	238°00	514°90
180°00	101°13	210°00	248°00	240°00	540°68
182°00	107°89	212°00	261°95	242°00	567°62
184°00	115°01	214°00	276°78	244°00	595°76
186°00	122°54	216°00	292°13	246°00	624°99
188°00	130°39	218°00	308°35	248°00	655°25
190°00	138°58	220°00	325°24	250°00	686°53
192°00	147°40	222°00	343°11	252°00	719°25
194°00	156°62	224°00	361°56	254°00	753°84
196°00	166°07	226°00	380°92		

The results are not in agreement with those of Jaquerod and Wassmer, whose vapour pressure curve cuts that obtained by the author in the neighbourhood of 215° and 240°, the greatest divergence amounting to about 1°0'. Moreover, in the data presented no discontinuity is observed on plotting according to the Ramsay-Young rule: the line is almost straight down to 190°, and below this temperature curves off gradually and smoothly in the usual way, that is, the ratios increase more and more rapidly as the temperature falls.

*Aniline.*—The aniline was purified by repeated distillation and was frequently removed from the apparatus and replaced by fresh portions.

The experimental points are given in Table III. Smoothed values were obtained as described for diphenyl, and are given in Table IV. The results

TABLE III.  
ANILINE—EXPERIMENTAL POINTS.

T° C.	P (mm.).	T° C.	P (mm.).	T° C.	P (mm.).
91°60	30°14	111°60	70°74	128°27	136°09
95°80	36°80	112°75	74°78	129°20	140°67
99°40	43°41	113°40	78°15	129°85	143°69
101°70	47°60	114°50	81°05	131°60	152°95
102°00	49°47	115°65	84°94	134°10	166°70
102°80	50°90	117°68	90°61	135°10	172°69
103°90	54°22	118°70	94°27	140°60	210°42
104°90	54°50	119°10	96°31	141°50	214°30
105°60	55°51	121°85	106°84	142°25	222°37
106°60	58°87	122°52	110°57	145°40	247°93
108°40	63°44	123°82	115°59	147°90	264°52
108°80	64°41	124°80	118°52	150°60	291°43
109°80	66°12	126°00	124°47	—	—

TABLE IV.  
ANILINE—SMOOTHED VALUES.

T° C.	P (mm.).	T° C.	P (mm.).	T° C.	P (mm.).
96·00	37·43	116·00	85·58	134·00	166·41
98·00	40·69	118·00	92·47	136·00	178·46
100·00	44·53	120·00	99·80	138·00	191·15
102·00	48·39	122·00	107·68	140·00	204·95
104·00	52·66	124·00	115·99	142·00	219·15
106·00	57·25	126·00	124·88	144·00	234·53
108·00	62·18	128·00	134·36	146·00	250·58
110·00	67·46	130·00	144·42	148·00	267·64
112·00	73·09	132·00	155·12	150·00	285·81
114·00	79·13	—	—	—	—

do not agree with those of Kahlbaum. The Ramsay-Young graph shows a smooth curve, the curvature being in the usual direction and more pronounced at lower temperatures. The line is nearly continuous with that of Beckmann and Liesche.

In conclusion, the author wishes to express his thanks to Professor R. Whytlaw Gray for suggesting the research, and for the kindly interest he has taken throughout the work.

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## A METHOD OF MEASURING VARIATIONS OF ELECTRICAL RESISTANCE FOR THE DETERMINATION OF THE THERMAL EQUILIBRIUM DIAGRAM OF AN INTER-METALLIC SYSTEM.

BY F. H. JEFFERY.

*Received 23rd March, 1927.*

Electrolytic copper and Johnson and Matthey's best tin were used. The mass of alloy was of the order of 400 grams and was contained in a Battersea round D. The temperature was measured by a chromel-alumel couple. The arrangement of the leads and furnace for measuring temperature and resistance is shown in Fig. 1. A silica tube containing the couple is at R, for the measurement of changes in electrical resistance two fine silica tubes, Q, Q, were arranged to dip into the alloy and molybdenum leads of diameter 1 mm. projected about 3 mm. through them into the metal. These leads were soldered at their cooler ends to copper leads and the junctions so formed were insulated by glass tubes and put in ice in a thermos flask as for a thermo-couple. The furnace consisted of a Fletcher fireclay envelope A, an iron cylinder B wound with ni-chrome wire insulated with asbestos tape, air gaps being left between the fireclay envelope, the heating element and the Battersea crucible, with asbestos rope on the top of these gaps. With this arrangement it was possible to maintain rates of heating and of cooling in the neighbourhood of transition points such that the temperature-time curves were sensibly rectilinear.

Two methods were used for measuring the variations of electrical resistance and of temperature: one (a) was a null-method for which Callendar

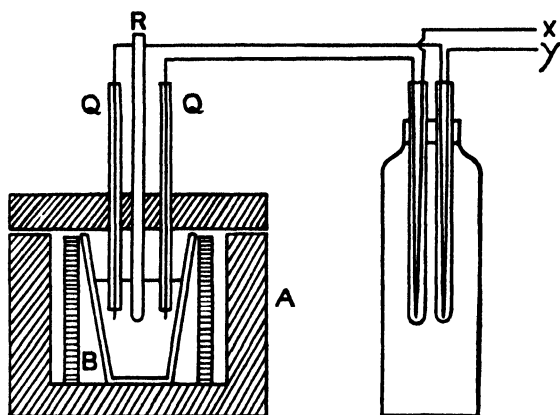


FIG. 1.

recorders were necessary: the other (b) involved a "back *E.M.F.*" method of measuring temperature and the measurement of variations of resistance by means of the current through a galvanometer of the type designed by Ayrton-Mather.

(a) Two Callendar recorders were used. These instruments were adjusted so that the motion of the two drums was synchronised.

One recorder was used for the measurement of change of resistance with time of cooling.

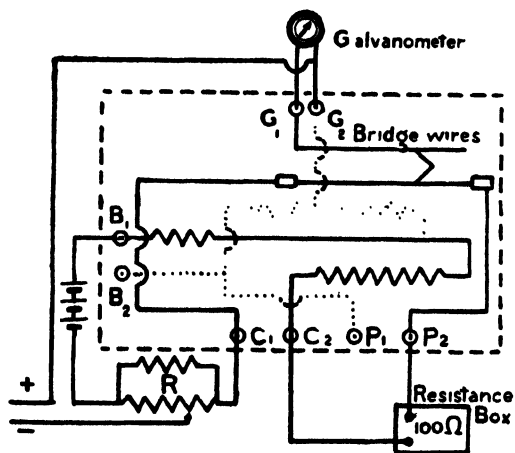


FIG. 2.—R, Potential divider consisting of twenty  $0.1 \Omega$  coils shunted with  $1 \Omega$ .

For this no connections inside the instrument were cut, but the bridge wire was shunted with a small resistance. The recorder was connected to the points X, Y, as for a platinum resistance pyrometer using quadruple flux except that in series with the C.C. leads there was a low resistance rheostat of total resistance 2 ohms and in series with the P.P. leads, a resistance coil of roughly 10 ohms. For any required temperature the rheostat could be so adjusted that the pen on the recorder

started at the right of the centre of the drum. The sensitivity for variation of the resistance of the alloy with temperature depends on the shunt and also on the moments of inertia of the moving parts of the recorder. The resistance of the shunt could be adapted to the series of alloys to be investigated. On the recorder a resistance of  $9.5$  ohms was used permanently in the C.C. arm of the bridge.

For the continuous measurement of the variation of temperature with time of cooling a second recorder was used. This instrument had to be modified so as to act as a potentiometer. The arrangement is shown in Fig. 2.  $G_1G_2$  are the galvanometer terminals, the wire leading from  $G_2$  to the junction of the two bridge coils was disconnected from  $G_2$ ; this was the only change necessary as far as the internal arrangements of the recorder were concerned. The positive end of the thermocouple was connected with  $G_2$  and the negative end with the sliding contact-maker of R. The couple was calibrated by means of standard freezing-points; for one and the same temperature it was always possible to find two positions of the pen by adjusting the contact-maker of R at successive coils. It was usually possible to find three and sometimes four positions of the pen for the same freezing-point. By these means the resistance of successive coils of R could be expressed in terms of lengths of the platinum wire of the recorder, and temperatures could be given in terms of inches or centimetres of this platinum wire.

For such measurements of temperature the constancy of the *E.M.F.* of the battery could be checked and the requisite correction made as follows: let  $l_M$  inches be the reading of the temperature of the standard metal M at the time when the calibration curve was drawn and  $l'_M$  inches that at the time of checking,  $l$  inches the corrected reading of the temperature required and  $l'$  inches the actual reading, E and E' being the corresponding *E.M.F.*'s of the battery—

$$l = \frac{E'}{E} \cdot l' = \frac{l_M}{l'_M} \cdot l'$$

$$\text{correction} = l - l' = \frac{l'_M - l_M}{l'_M} \cdot l' \text{ inches.}$$

Also it was often possible to bracket the temperature observed by recording two standard temperatures on the drum and hence to calculate the temperature, the calibration curve for the chromel-alumel couple obtained by this null method being rectilinear from  $100^\circ \text{C.}$  to  $700^\circ \text{C.}$

From the results traced on the two drums a curve giving the change of resistance as a function of the temperature could be drawn. The change of resistance given by the first recorder was expressed in inches or centimetres of the platinum wire of this instrument.

This method is applicable to temperatures at which the alloy is liquid down to any temperature below the solidus. The method does not give the absolute value of the resistance at any instant during cooling nor heating, but does show the rapid change of curvature in the resistance-temperature curve when a new phase is formed.

The conduction of electricity in the alloy is in "three" dimensions and the mass of metal used is large; this is necessary inasmuch as the electrical resistance of a heterogeneous system and particularly of a system where the order of heterogeneity is changing must be of the nature of a statistical measurement.

The advantage of this method with the two recorders is that it is a null method which can be used with very slow cooling, but the current through the alloy cannot be varied at will except within a narrow range.

(*b*) This alternative method does not necessitate such expensive apparatus though it gives a continuous record, but two observers are needed. The apparatus for measuring the variation of electrical resistance with time of

cooling is shown in Fig. 3. The Ayrton-Mather galvanometer was arranged so that its mirror reflected a spot of light on to a glass screen covered with squared paper which moved upward with uniform velocity, this velocity could be adjusted to the rate of cooling; a curve was traced on the paper by following the spot—which moved from the right-hand side of the screen to the left hand, the abscissæ measured from an origin close to the left-hand side being directly proportional to the change in resistance of the alloy. By means of the rheostat *S* it was always possible to trace a curve through any required temperature. The moving screen was designed many years ago by Heycock. The temperature was measured by a chromel-alumel couple fitted with a back *E.M.F.* arrangement; this consisted of a 10,000 ohm coil in series with a dial resistance box and a 2-volt accumulator; the thermo-couple circuit was connected with the terminals of the resistance box.

As the galvanometer spot passed each centimetre mark on a scale fixed in front of the galvanometer an observer gave notice of this and a mark was made on the resistance-time curve traced on the moving screen. From

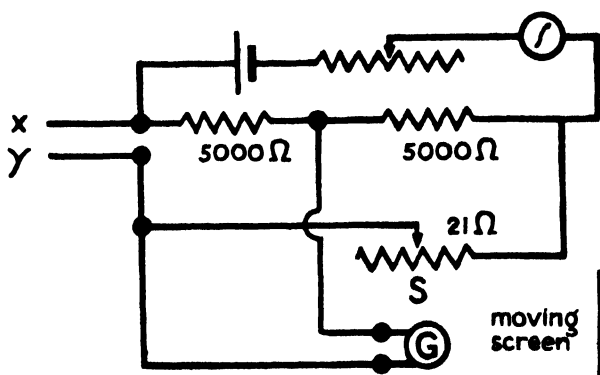


FIG. 3.

these observations a curve giving change of resistance as a function of the temperature could be constructed.

The advantage of this method is that the moment of inertia of the Ayrton-Mather galvanometer coil is small and in consequence changes in the resistance of the alloy can be followed with very little lag; also the current through the alloy can be varied through a wide range. By such means it can be determined whether perturbations due to irreversible heat effects may be confusing the observations. For such currents as were used—currents up to 0.5 amp. no such difficulties were found.

#### Application to a Portion of the Series of Copper-Tin Alloys in order to examine the effect of the rate of cooling on the accuracy of the result.

In order to test this method copper-tin alloys of compositions from 40 atomic per cent. tin to 98 atomic per cent. tin were examined.

Isihara examined the complete series of copper-tin alloys by an electrical resistance method using a potentiometer, the rate of cooling adopted by him being 0.67° C. per minute; for temperatures below the solidus he used rods, for temperatures above he arranged two silica tubes dipping into the

alloy contained in a crucible and measured the resistance of two cylinders of alloy surrounded by these tubes. In the apparatus described previously no such differentiation of a portion of the alloy was made.

In the following tables results obtained by method (a) and by method (b), with faster cooling, are given; the results obtained by Heycock and Neville for the same alloys are given as a standard of comparison; the letters refer to the Heycock and Neville diagram of 1903, the phrase "Isihara line" refers to the line of points at 180° C. as given by Isihara in his paper of 1924.<sup>1</sup>

METHOD (a).

	Liquidus.	E <sub>2</sub> G.	E <sub>3</sub> H'H.	H'H''.	E <sub>4</sub> H''L.	Isihara Line.
40 atomic per cent. Sn	653	633	414	370	227	—
48 " " "	621	—	408	266	226	—
55 " " "	590	—	411	236	227	—
60 " " "	565	—	414	no point	227	—
70 " " "	517	—	409	—	227	—
84 " " "	433	—	407	—	227	—
88 " " "	400	—	no point	—	—	—
90 " " "	374	—	no point	—	227	—
98 " " "	244	—	no point	—	227	—

*Time of Cooling.*—Through the liquidus and E<sub>2</sub>G the rate of cooling was 0.4° C. per minute. The alloy was then slowly cooled and kept at an approximately constant temperature during 16 hours; this temperature was about thirty degrees above the E<sub>3</sub>H'H line. The rate of cooling through this line was again 0.4° C. per minute, and this rate was maintained until the temperature had dropped below the H'H'' line.

All the alloys examined gave well-marked eutectic arrests: the term seems appropriate in that in all the resistance-temperature curves the portions at the eutectic were rectilinear and parallel to the resistance axis.

The Isihara line was examined both with slower rates of cooling and with faster rates. From 0.2° C. per min. to 0.5° C. per min. no points corresponding to this line were found. In the rate of cooling 1° C. per min. a sharply defined point was found at 183° C. for the 40 atomic per cent. tin alloy.

METHOD (b).

Approximate Rate of Cooling through these Points.	Liquidus, 2.5° C./min.	E <sub>2</sub> H'H., 2.5° C./min.	H'H'', 2° C./min.	E <sub>4</sub> H''L.	Isihara Line, 1.5° C./min.
43 atomic per cent. Sn	625°	402°	322°	224°	176°
46 " " "	610°	402°	303°	225°	179°
48 " " "	610°	403°	274°	224°	177°
50 " " "	602°	403°	260°	225°	177°
52 " " "	598°	401°	249°	225°	179°
55 " " "	586°	402°	234°	227°	181°
60 " " "	565°	402°	no point	226°	178°
70 " " "	520°	402°	no point	225°	178°

The curves obtained by this method were for the greater part on a more open scale. They were in other respects similar to those of method (a). The points on the Isihara line were well marked.

<sup>1</sup> Isihara, *J. Inst. Met.*, 1924, 1, 315.

## RESULTS OF HEYCOCK AND NEVILLE.

Alloy Atomic Per Cent. Tin.	Liquidus.	$E_2G$ .	$E_3H'H$ .	$H'H''$ .	$E_4H''I$ .	Isihara Line.
40	651°	630°	400°	no point	(226)	This was not examined
43	636°	—	400°	no point	(226)	
46	623°	—	400°	about 360°	(226)	
48	615°	—	400°	about 290°	(226)	
50	606°	—	400°	about 226°	226	
52	598°	—	400°	no point	226	—
55	586°	—	400°	no point	226	—
60	565°	—	400°	no point	226	—
70	519°	—	400°	—	226	—
84	429°	—	400°	—	226	—
90	374°	—	no point	—	226	—
98	—	—	no point	—	226	—

In this table the figures for the liquidus were obtained by interpolation from the results given in "The complete freezing-point curves of binary alloys," *Phil. Trans.*, 1896, the rest from the Bakerian Lecture of 1903.

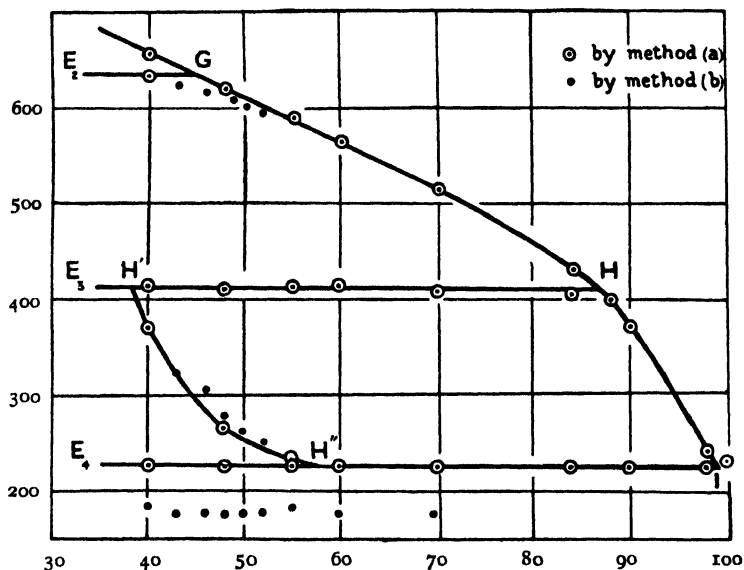


FIG. 4.

Fig. 4 is a thermal equilibrium diagram as obtained by method (a). Points obtained by faster cooling, using method (b), are also shown when they differ from those by (a).

## Discussion of Results.

The diagram as obtained by the slow cooling method (a) is in substantial agreement with the work of Heycock and Neville; but in this diagram the  $E_3H'H$  line is at 411° C. instead of being at 400° C. as given by them, and there is a break in the liquidus at H which was not detected by their method with the platinum resistance pyrometer; the point H' appears to be on an ordinate corresponding with about 38 atomic per cent. tin and

H'' on one corresponding with about 58 atomic per cent. tin, there being no point on H'H'' for 60 atomic per cent.

The diagram is not in accord with that given by Ishihara; his diagram has a line of points at 180° C. and shows H'H'' as a straight line parallel to the temperature axis,  $E_3H'H$  is shown at 400° C. It seems probable that the results obtained by Ishihara's electrical resistance method differ from those obtained by the method described partly because of his rate of cooling—0.67° C. per minute—but still more by virtue of his finding the change of resistance of the alloys by using rods for solids and small cylinders enclosed by silica tubes for alloys containing a liquid phase; it may be that this method does not give trustworthy results for heterogeneous conductors in a state of progressive change if it be correct to regard the resistance of such a system as of the nature of a statistical valuation.

The effect of the rate of cooling is shown by a comparison of the results obtained from method (a) and from method (b).

*The liquidus.* The points from slow cooling are almost in complete agreement with those given by Heycock and Neville, the points from (b) are somewhat low beyond 600° C. though they are in better agreement at lower temperatures. If the solid from the liquid alloy be first formed as a highly disperse phase a change of electrical resistance would be produced more rapidly than a change of temperature, and this would account for approximately accurate results even with rapid cooling. *The line H'H''.* This boundary separates a system containing a liquid phase from one which does not contain any liquid phase when the cooling is sufficiently slow, but which does contain it as an intrusive phase for the rate 0.4° C. per minute. It is surprising how closely the points obtained by rapid cooling (b) agreed with those by method (a); undoubtedly the latter method is the more trustworthy. Heycock and Neville stated that they did not investigate the line H'H'' fully but they made it slope: it is difficult to reconcile their work with the results of Ishihara. It seems probable that if the new phase were formed in a disperse condition the results of the rapid cooling would be explicable. *The eutectic line  $E_4H''I$ .* The results by slow cooling method (a) gave 227° C., Heycock and Neville gave 226° C., the more rapid cooling of method (b) gave 225° C. It is to be noted that well-marked eutectic "arrests" by (a) were given by alloys from 40 atomic per cent. tin to those of 55 atomic per cent. tin: this result does not agree with the conclusions of Ishihara who gives no eutectic line beyond 48 atomic per cent. tin. Heycock and Neville give eutectic arrests from 40 atomic per cent. to 50 atomic per cent. and onwards. Heycock and Neville showed that *much* depended on the rate of cooling through the  $E_3H'H$  boundary. *The line  $E_3H'H$ .* The slower cooling of method (a) gave the line at 411° C.  $\pm 3^\circ$  C. The deviation is too great; the cooling should have been slower; faster cooling seems worthless even with a galvanometer of low moment of inertia. Heating curves were not made; in the light of what Heycock and Neville state in their account of their micrographic analysis these curves might have been more trustworthy. The platinum resistance pyrometer might well give a low result owing to the sheath. *The Ishihara line.* The existence of this line involves difficulties in the interpretation of a thermal equilibrium diagram which may contain it. The results of Ishihara's work appear to be due to the rate of cooling and to his mode of assessing the electrical resistance of his alloys. Undoubtedly this question needs further investigation.

Haughton<sup>2</sup> examined alloys containing 55 per cent. tin, 61 per cent.

<sup>2</sup> *J. Inst. Met.*, 1921, I, 321.

tin, 63 per cent. tin by an electrical resistance method, the alloys being in silica tubes (Broniewski), his rates of cooling and of heating were such that from  $100^{\circ}\text{C.}$  to  $250^{\circ}\text{C.}$  the time taken was about seven hours. He obtained evidence for points below  $227^{\circ}\text{C.}$  The curves obtained by method (a) gave no indication of these points.

This electrical resistance method with slow cooling appears to be very sensitive to the formation of a new phase, but there must be a superior limit to the rate of cooling; though this is not necessarily the same for every alloy. Some preliminary experiments have been made with other intermetallic systems which have been well examined, in order to see how the method can fix the solidus when solid solutions are formed. It gave results in agreement with the results of micrographic analysis. This method cannot supersede micrographic analysis, but it can lessen the labour involved.

### Application to the Determination of the Higher Transition Point of Tin.

The higher transition point of tin was examined by this method. Purest tin from Messrs. Pass was used. It was kept molten at  $240^{\circ}$  during 18 hours and was then cooled at the rate of  $0.5^{\circ}\text{C.}$  per minute. A well-marked break on the resistance-temperature curve was obtained at  $162^{\circ}\text{C.}$

The metal was then kept at  $140^{\circ}\text{C.}$  for about 18 hours and then heated at the rate of  $0.4^{\circ}\text{C.}$  per min.; an equally well-marked break occurred at  $162^{\circ}\text{C.}$

For a rate of cooling of  $0.9^{\circ}\text{C.}$  per min. a point was obtained at  $161^{\circ}\text{C.}$  and for a rate of heating of  $0.8^{\circ}\text{C.}$  per min. a point was obtained at  $163^{\circ}\text{C.}$

### Summary.

1. A continuous method of measuring the change of electrical resistance of an alloy with change in temperature has been described.

2. The method has been applied to the series of copper-tin alloys from 40 atomic per cent. tin to 98 atomic per cent. tin. The results are in almost complete agreement with those obtained by Heycock and Neville, but not in accord with those obtained by Isihara, nor with those obtained by Haughton.

3. The higher transition point of tin has been determined by this method to be  $162^{\circ}\text{C.}$

The author is once more indebted to the Goldsmith's Reader in Metallurgy, Col. C. T. Heycock, F.R.S. During most of the experiments made by method (b) he had the honour of working with him; sometimes Col. Heycock drew the curves on the moving screen which he had invented and sometimes he called the temperatures. In addition the author had the peculiar advantage of his advice on a variety of questions arising from a study of the copper-tin system.

The author is also grateful to Mr. W. R. Nimmo, B.A., Emmanuel College, Cambridge, and to Mr. A. R. Raper, B.A., Sidney Sussex College, Cambridge, for kind and efficient help at many times.

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# ON THE PERSISTENCE OF POTENTIAL AT A MERCURY CATHODE ON OPEN CIRCUIT.

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In order that the continuous deposition of hydrogen ions may occur at a metallic cathode, it is necessary that the potential be considerably more negative than that of a reversible hydrogen electrode in the same electrolyte. In general, on breaking the polarising circuit this overpotential decays very rapidly, reaching a low value in a few seconds. Several forms of commutator have been devised for measuring this rapidly falling potential. The more recent are these of Glasstone<sup>1</sup> and Newberry,<sup>2</sup> the latter using a cathode ray oscillograph which has recorded the fall of potential  $10^{-4}$  seconds after the circuit was opened. All these methods show a rapid drop in the back *E.M.F.* In the experiments to be described it was possible to get a persistence of this potential for a much longer period, in some cases for several hours, and it is shown that this back *E.M.F.* is due to traces of negative metal impurities which are deposited at the cathode during electrolysis. Impurities of the order of  $< 10^{-6}$  g. equivalents are sufficient to cause a marked persistence of the potential and, under most experimental conditions, impurities are present and can be deposited in this amount. Since the potential of the cathode on open circuit is controlled by these negative metals it is apparent that the measurement of this potential and its rate of decay can throw little light on true hydrogen overpotential.

## Preliminary Experiments.

After the electrolysis of *N*/1 sulphuric acid in a glass beaker, using a platinum anode and a pool of mercury as cathode with a high current density, the potential of the cathode<sup>3</sup> on opening the circuit frequently takes several minutes to fall to that characteristic of mercury and acid. For example:—

Electrolysis continued for 15 minutes at current density 1 amp./cm.<sup>2</sup>  
Electrolyte *N*/1  $H_2SO_4$ . Diameter of cathode 3 cm.

Potential on closed circuit	— 1.65 volts.
" " open " after $\frac{1}{4}$ min.	— 0.84 volts, after 3 min. — 0.40 volts.
" " " " $\frac{1}{2}$ " "	— 0.75 " " 4 " — 0.2 "
" " " " $1\frac{1}{2}$ " "	— 0.60 " " 30 " + 0.3 "

<sup>1</sup> *J. Chem. Soc.*, 125, 2414, 2646.

<sup>2</sup> *Proc. Roy. Soc.*, 107, 486, 1925.

<sup>3</sup> Cathode potentials are measured by the direct method, a glass tube drawn out to a fine capillary and just meeting its image in the cathode surface making contact through sat. KCl with a saturated calomel electrode. (+ 0.248 volts on hydrogen scale.) All potentials are given against this calomel electrode. No correction is applied for the diffusion potential at the KCl electrolyte boundary.

The mercury used was re-distilled in a current of air and twice redistilled in vacuo. The acid was Cumming Smith, C.P., and distilled water was used throughout. All apparatus previous to use was washed in strong chromic acid and distilled water.

The characteristic potential of fresh mercury and sulphuric acid is + 0.3 volts to + 0.4 volts. Prolonged electrolysis, high current density and low temperature favour this persistence of potential, but its occurrence is erratic. Under apparently identical experimental conditions it may or may not occur.

To investigate this further the apparatus was modified so as to exclude oxygen from the cathodic region, the cell consisting of two pyrex beakers

Decay of back *E.M.F.* on open circuit.  
 $N/1 H_2SO_4$  electrolyte.  
 After electrolysis 0.6 amps for 2 hours. Cathode area, 5 cm.<sup>2</sup>

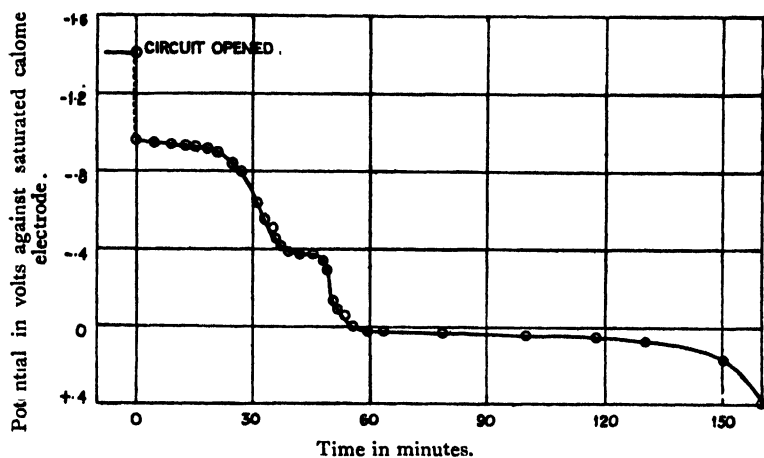


FIG. 1.

connected by a glass U tube, one containing the platinum anode and the other a porcelain crucible or a watch glass holding the mercury cathode. With this arrangement the persistence of potential after electrolysis was much more marked and in some cases extended over several hours. Fig. 1 is a typical curve, showing the fall of potential with time on open circuit. All these curves show the same characteristics, *viz.*: A very rapid initial drop

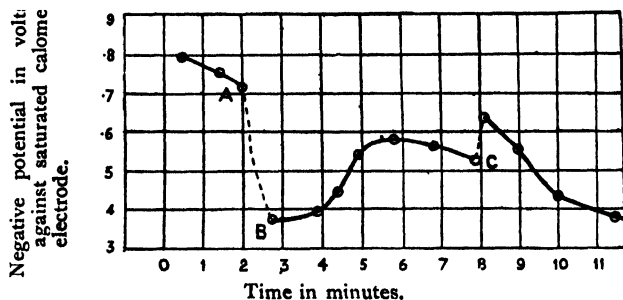


FIG. 2.

from - 1.4 volts (approx.) to - 0.95 volts followed by a slow decay down to the potential characteristic of mercury with marked pauses at potentials of approx. - 0.95 volts, - 0.35 volts and + 0.1 volts.

In Fig. 2 is shown the effect of stirring on the rate of fall of potential. It represents a portion of the decay curve after the circuit has been open for several minutes. At the point A the electrolyte is gently stirred, at B

the stirring is stopped, at C the surface of the cathode is slightly disturbed with a glass rod.

It will be seen:—(a) that stirring the electrolyte causes a sudden drop in the potential but on cessation the potential rises again to a value which is approximately the same as the potential would be had no stirring occurred, (b) disturbing the cathode causes an increase in the potential, (c) that stirring both cathode and electrolyte greatly increases the rate of fall.

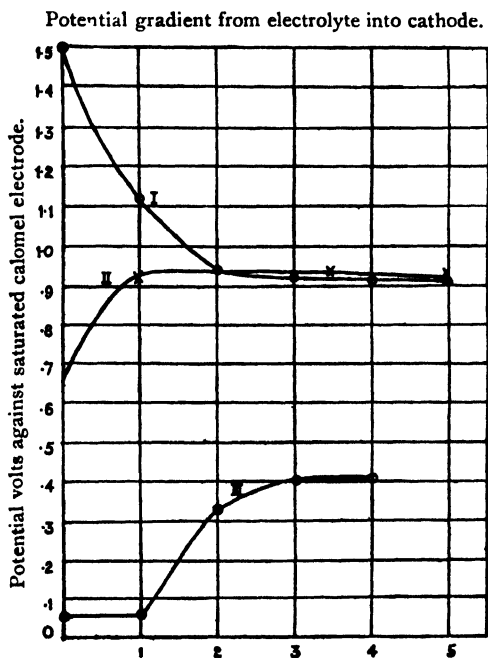
For example, two cathodes electrolysed under identical conditions behaved as follows:—

Cathode and electrolyte stirred.	Time to fall from $-0.95$ volts to $+0.3$ volts was 3 mins.
No stirring . . . . .	Time to fall from $-0.95$ volts to $+0.3$ volts was 50 mins.

### Experiments with Exploratory Tip.

To investigate the conditions existing within the body of the cathode, the measuring tip (drawn out very fine) is mounted on a screw so that it can be lowered to known distances beneath the mercury surface. The cathode is 1 cm. deep by 2.5 cm. in diameter.

With fresh mercury the potential on open circuit is the same above and below the surface, *viz.*,  $+0.3$ . On closing the circuit the potential at the surface instantaneously attains its equilibrium value of  $-1.4$  volts (approx.) with a current of .25 amps. passing. Below the surface however (tip immersed 0.6 cm.) the behaviour is different. The potential rises slowly after 1 sec.  $-0.2$  volts, after 3 sec.  $-0.55$  volts, after 10 sec.  $-0.7$  volts rising in three minutes to an equilibrium value of  $-0.95$  volts. This potential of  $-0.95$  volts is identical with that shown by a cathode on first opening the polarising circuit.



In Fig. 3 is shown the potential gradient from the surface to the interior of the cathode under varying conditions. Curve I shows the conditions during electrolysis after the current has been flowing some time. The potential at the surface is  $-1.5$  volts, while throughout the mass of the cathode it is  $-0.95$  volts. The intermediate point is difficult to interpret. At this point the tip is making a depression in the mercury and it may not actually be below the surface, the lower reading being simply due to the smaller current density obtaining

FIG. 3.

in this depression. There is very possibly a sudden transition between the  $-1.5$  volts and the  $-0.95$  volts. Curve II. shows the condition a few seconds after opening the circuit. The potential of the surface has fallen considerably, while no appreciable drop has occurred within the cathode. Curve III. shows the condition one hour after the circuit is opened. The potential of the whole cathode has decreased, and shows a definite gradient from the interior to the surface.

### Discussion.

Consider the graph in Fig. 1. There are, broadly speaking, two features which require explanation—(a) the initial rapid drop to  $-0.95$  volts. This will be considered later: (b) the slow decay from this potential. An explanation consistent with the experimental results is that the persistence of potential is due to an accumulation of electromotively active material which is dispersed throughout the whole mass of the cathode. The potential of the cathode, when in equilibrium, under these conditions is  $-0.95$  volts. The rate of decay of this "amalgam" will be limited by two factors:—(i) the rate at which it is removed from the surface layers: (ii) the rate at which it can diffuse to the surface from the interior of the cathode.

Stirring the electrolyte will speed up (i) and the potential will fall, but on standing, the diffusion of fresh material to the surface will cause the potential to rise again. Stirring the cathode will bring fresh amalgam to the surface, causing an increase of potential—see Fig. 2. Stirring both electrode and electrolyte will continuously bring fresh amalgam in contact with electrolyte and so hasten the decay.

On first establishing the circuit at a fresh Hg cathode, this active material is deposited on the surface layers, but it requires time to diffuse into the body of the cathode so that the potential beneath the surface rises slowly to the characteristic equilibrium value of the amalgam, *viz.*  $-0.95$  volts. On continued electrolysis the whole body of the cathode attains this potential. When the circuit is opened rapid decay from the surface layers occurs and the potential falls. Within the cathode the decay is limited by the rate of diffusion to the surface so that the drop in potential occurs more slowly. This is well illustrated by Curves II. and III., Fig. 3.

These experiments lead to the conclusion that the persistence of back *E.M.F.* is due to the slow decay of electronegative material permeating the whole cathode. This material must be either (i) active hydrogen, *i.e.* atomic hydrogen or a hydride dissolved in the mercury, or (ii) negative metals (*e.g.*, NaMg) present in small quantities as impurities in the electrolyte or dissolved from the glass vessels.

This point has an important bearing on the theories and measurement of overpotential, and the work was continued in order to throw more light on the behaviour of this active material.

### Discharge on Activated Cathode.

Hydrogen is deposited at the cathode until it shows on open circuit the equilibrium potential of  $-0.95$  volts. The cathode is then connected through a micro-ammeter and resistance to a hydrogen electrode immersed in the electrolyte. The current which flows during the fall of the potential of the cathode to that of the hydrogen electrode is supplied by the decay of the active material. The current is measured every half minute and plotted against time. The area under this curve represents the quantity of

electricity yielded by the active material. The following table shows the effect of varying the resistance in the circuit and of stirring :

Conditions.	Resistance in Circuit, (Ohms).	Time of Decay, (Minutes).	Coulombs Yielded.
No stirring	40,000	50	·002
" "	2,000	51	·03
" "	6	50	·05
Stirring	200	3½	·03
"	6	3½	·05

and indicates (i) the time of decay is independent of the resistance in the circuit, (ii) the current which flows increases with decreasing resistance, and (iii) stirring the cathode greatly reduces the time of decay. This behaviour is consistent with the views advanced in the previous section. The active material reacts very readily with the electrolyte, so that assisting the reaction electrolytically by shorting the cell, will have little effect on the rate of decay. The limiting factor is the rate of diffusion of material to the surface. Since the reaction proceeds rapidly from the mercury surface, the fraction of the total energy of reaction which will appear as electrical energy will depend on the resistance in the circuit. The lower the resistance the greater will this amount be, with correspondingly less appearing as heat.<sup>4</sup>

In any case, the minimum amount of active material (*i.e.* material whose potential is above the hydrogen electrode) present in the cathode can be calculated.

Quantity of electricity given up during discharge with minimum resistance in circuit = ·05 coulomb (approx.).

This is equivalent to  $\frac{·05}{96500} = 5 \times 10^{-7}$  gm. equivalents.

This is the minimum amount present in 65 gms. of mercury after the cathode has been subjected to prolonged electrolysis. Compare page 579.

### Nature and Deposition of Active Material.

It has been established that the persistence of potential at a mercury cathode after opening the circuit is due to electronegative material which permeates the whole cathode and that this must be either active hydrogen or negative metal impurities. As will now be shown the experimental evidence is in favour of the latter. The explanation offered for the phenomena observed is that small quantities (see page 580) of electronegative metals present in the solution are, under the conditions of electrolysis, deposited at the surface of the mercury cathode and there dissolved in it, forming a dilute amalgam. When the circuit is first opened the cathode assumes the potential of the most negative of these amalgams. The active metal dissolves from the surface of the cathode, leaving a more dilute and hence less negative amalgam. As the surface layer becomes exhausted of this impurity, the potential drops rapidly to that characteristic of the next when the process is repeated. If the cathode has been subjected to prolonged electrolysis so that the amalgam is dispersed throughout the cathode, the decay of potential is slower since fresh material is continually diffusing to the surface. To explain this persistence as due to active hydrogen it

<sup>4</sup> An attempt was made to measure the heat of decay of this amalgam by allowing the reaction to proceed in a Bunsen ice calorimeter and, from this, to estimate the quantity of active material present. The instrument in the form used was not sufficiently sensitive to detect any heat of reaction.

would be necessary to suppose the existence of several definite "hydrides" having the characteristic potentials at which the flattenings occur.

In general, high current density, low temperature and prolonged electrolysis favour the persistence of potential, but under apparently identical experimental conditions this persistence can occur to varying degrees. Experiment has shown that an important factor is the production in the immediate vicinity of the cathode of a layer of electrolyte of low hydrogen ion concentration. The mechanism of the deposition of possible impurities will be considered here.

In order that the continuous deposition of hydrogen ions and their evolution as gas may occur at a mercury cathode in dilute sulphuric acid it is necessary that the potential of the cathode be maintained at a value considerably more negative than that of a reversible hydrogen electrode in the same electrolyte. In this paper the mechanism of this overpotential is not considered. Under the experimental conditions employed, with  $N/1$  sulphuric acid electrolyte and a current density of  $0.04$  amps./cm.<sup>2</sup>, the cathode potential is approximately  $-1.4$  volts corresponding to an overpotential of approximately  $1.1$  volts. During electrolysis hydrogen ions are deposited on the cathode from the layer of electrolyte in its immediate vicinity, this layer being replenished by migration of hydrogen from the bulk of the electrolyte, by dissociation of any undissociated acid, by diffusion and by a stirring of the electrolyte caused by gas evolution or flow of solution. Under the influence of the electric field the relatively slow moving metallic impurities are also migrating up to this layer. If the cathode potential is above the deposition potential<sup>5</sup> of the metallic impurity, it will be continuously deposited and will diffuse through the mass of the cathode. If, however, the cathodic potential is not sufficiently negative the metallic ions will accumulate in this layer; there will, of course, always be present on the cathode surface a sufficient concentration of the metal to be in equilibrium with its ions in the electrolyte layer. So that the impurities having a deposition potential below  $-1.4$  volts (*viz.*: As, Pb, Zn, see page 580), are plated out and the potential of the cathode beneath the surface rises slowly, as the metals diffuse through, from that of mercury, to that characteristic of the most negative of them (*viz.*: Zn at  $-0.95$  volts).

Continued electrolysis at high current density<sup>6</sup> results in a diminution of the hydrogen ion concentration in the electrolyte layer in immediate contact with the cathode,<sup>7</sup> since hydrogen ions are being rapidly removed from it by deposition and but slowly replenished by migration, diffusion, etc. At the same time the impurities, which cannot deposit, are accumulating in this layer. The presence of this dilute layer is shown by a marked increase in the resistance of the cell, although the bulk of the electrolyte in the cathode beaker may be still strongly acid and by an increase in the potential of the cathode. A very slight disturbance of the electrolyte is sufficient to destroy this layer.

If the conditions of electrolysis have been such that the impurity could continuously deposit and permeate the cathode, it will take a long time to redissolve for it can diffuse but slowly to the cathode surface; if, however, the time of electrolysis has been short or the potential has not been

<sup>5</sup> That is, above the deposition potential at a mercury cathode. If the metal is capable of forming an amalgam this will be considerably lower than that required for deposition of the pure solid metal.

<sup>6</sup> If the current density is too high the rapid evolution of gas bubbles stirs the electrolyte and hinders the formation of the dilute layer.

<sup>7</sup> See Sand, *Phil. Mag.*, 6, 45 (1901).

sufficient for the continuous deposition of the impurity so that it is only present in the surface layer of the cathode, the time for its removal may be very short. This is the explanation offered for the decay curve, Fig. 2. The initial sudden drop of potential ( $-1.4$  to  $-0.95$ ) is due to the rapid resolution of minute amounts of alkali metals from the cathode surface. The potential of the cathode ( $-1.4$  volts) was not sufficiently negative for the continuous deposition of these metals, so that they were only present on the mercury surface in the concentration required for equilibrium at the potential of  $-1.4$  volts. The slow decay from  $-0.95$  is due to the gradual resolution of the metals which could deposit at this potential.

The rate of fall of potential on open circuit is also greatly influenced by the presence of this dilute layer. Resolution consists of the deposition of a hydrogen ion on the cathode surface and the passage into solution of an equivalent metal ion. If the hydrogen ion concentration of the layer is low, this reaction will be slow. The experimental work has shown this to be a very important factor. If the hydrogen ion concentration of the electrolyte in contact with the cathode is high (say  $N/1$ ) the rate of resolution will be very rapid, the potential of the surface layer falling in a few seconds to a low value, even though the interior of the cathode is still rich in the impurity and gives a high negative potential.<sup>8</sup> In most experimental work the strength of electrolyte, time of electrolysis and movement of solution are such that the hydrogen ion concentration of the electrolyte in contact with the cathode is not very low. This explains the rapid fall of potential which is generally observed. In work with the commutator in particular, the time during which the circuit is closed is usually short so that only a small quantity of impurity is deposited and also the hydrogen ion concentration of the electrolyte layer is decreased but little. Hence the observed decay of potential on open circuit is very rapid.

### Production of Dilute Layer.

In the deposition of hydrogen at the mercury cathode under the conditions previously described the gas is evolved as large bubbles ( $0.1$  mm. to  $1.0$  mm.) at the bright mercury surface, the potential on closed circuit with the tip just on the surface being about  $-1.5$  volts. After prolonged

<sup>8</sup> If the tip is lowered beneath the mercury surface, it is isolated from the main cathode and electrolyte and the potential difference measured is that between the electrolyte in the tip and the small area of mercury at its mouth. Since the tip is drawn very fine, the mercury, owing to capillary depression does not enter it. If the electrolyte in the tip is dilute, the rate of removal of active material from the surface of this small mercury area is comparatively slow, so that diffusion from the large mass of Hg surrounding it is capable of keeping its composition sensibly the same as the surrounding mercury. This is shown by the fact that moving the tip to and fro in the cathode, or raising it to the surface and redipping it, causes no appreciable change in the potential reading. So that measurements made under these conditions give the true potential difference between the dilute electrolyte and the mass of mercury in the vicinity of the tip. Owing to the high resistance of the dilute electrolyte in the tip, the potentiometer circuit is insensitive and potentials are measured to  $\pm 25$  m.v.

If, however, the electrolyte in the tip is strong ( $N/1$   $H_2SO_4$ ) and the base of the tip is large, the active material is removed from the area at the mouth more rapidly than it can be supplied by diffusion and the potential is lower than that characteristic of the surrounding mercury. Moving the tip to and fro causes a rise in the potential. Moreover, even when the tip is stationary marked fluctuations may be observed in the potential as the material is alternately removed and renewed. The potentiometer circuit is sensitive in this case since the conductivity of the electrolyte in the tip is high. It is obvious that potentials measured under this condition are not a true indication of the composition of the surrounding mercury. In general measurements were made under the former conditions, the insensitivity of the potentiometer circuit being an indication of this.

electrolysis, however, a marked change occurs, the potential at the surface rising to 2.2 volts.<sup>9</sup> At the same time the potential within the body of the cathode increases from - 0.95 to - 1.7 volts (approx.). The character of hydrogen evolution changes to clouds of very small bubbles and frequently patches of scum of metallic appearance occur on the cathode surface. At the same time the resistance of the cell increases, causing a decrease in the polarising current. This decrease may be slight, *e.g.*, in one case it fell from .22 amps. to .18 amps. (cathode area 5 sq. cms.) or it may be very considerable, *e.g.*, from .2 amps. to .0001 amps. for the same applied voltage. This increase in resistance is also shown by a decrease in the sensitivity of the potentiometer circuit indicating that the resistance between the measuring tip and the cathode has increased. The cathode is now in the "high potential" condition and is sufficiently negative to allow the deposition of metals such as Na and Mg.

This high potential condition can only occur when the hydrogen ion concentration of the electrolyte in the immediate vicinity of the cathode has fallen to a low value and since the bulk of the electrolyte in the cathode beaker is still acid (now  $N/20$ ), it is apparent that even on closed circuit this is an unstable state. Any slight disturbance of the electrolyte will bring fresh electrolyte in contact with the cathode surface causing rapid decomposition of the amalgam with consequent increased stirring due to rapid gas evolution, the potential falling in a few seconds to the normal value (*viz.* - 1.4 volts).

An interesting transition state between the two conditions has been observed. The cell had been subjected to prolonged electrolysis with a current of .15 amps. and the electrolyte in the cathodic beaker was approximately  $N/30$ . The potential of the cathode showed regular periodic fluctuations between the normal and high potential conditions. At the beginning of the cycle hydrogen in large "normal" bubbles was being evolved, the cathodic potential being - 1.4 volts. This hydrogen evolution gradually diminished and the potential of the cathode rose; after 25 seconds no visible evolution of hydrogen occurred and the potential of the cathode was - 2.0 volts. This condition was maintained for 10 seconds. Then, explosively, clouds of fine bubbles were evolved, the potential dropped suddenly to - 1.4 volts and the cycle was repeated. The polarising current remained approximately constant throughout at .15 amps. and the potential beneath the surface was - 0.95 volt (approx.). These cycles repeated with remarkable regularity for some hours and finally the high potential condition set in. During the early part of the cycle the layer is being depleted of hydrogen ions and the cathodic potential becoming more negative, so that increasing deposition of the impurity occurs. This deposition results in a depletion of the electrolyte layer with regard to the impurity and an increase in the solution pressure of the amalgam. Finally, the limit is reached and resolution commences. This causes hydrogen evolution with consequent stirring and a rapid drop of potential. The layer now is once more rich in the impurity and the cycle is repeated. It is probable that the clouds of fine bubbles evolved in the high potential condition are due to secondary hydrogen, *i.e.*, hydrogen evolved by the resolution of the alkali metal.

<sup>9</sup> Since the resistance of electrolyte is very high, a slight increase in the distance of the measuring tip from the cathode when the current is flowing causes a large increase in the measured potential. In the measurements given the tip just meets its own image in the Hg surface.

When the tip is beneath the surface it is immersed to a depth of about 3 mm.

### Fall of Potential on Open Circuit.

In Fig. 4 is shown the decay of potential on open circuit from this high potential condition, the tip being above the surface of the cathode.

The potential on first opening the circuit is sensibly the same as that given on closed circuit with the tip immersed, *viz.* :  $-1.7$  volts and from this it decays slowly to  $-0.95$  volt, the form of the curve after this being identical with that given by an electrode in the normal state.

*Artificial Production of Dilute Layer.*—To investigate this further the dilute layer was artificially produced. The anodic beaker and U tube were filled with  $N/1$   $H_2SO_4$  as before, but the cathodic beaker contained very dilute sulphuric acid ( $p_{H4}$ ). Owing to the high resistance of this only a small current can pass, but it was found that under these conditions the passage of a very small quantity of electricity is sufficient to produce the

Decay of back *E.M.F.* on O.C. from high potential condition.  
After electrolysis  $1$  amps for  $30$  hrs. cathode  $5$  cm.<sup>2</sup> Finally, electrolyte in cathodic beaker =  $N/20$   $H_2SO_4$ .

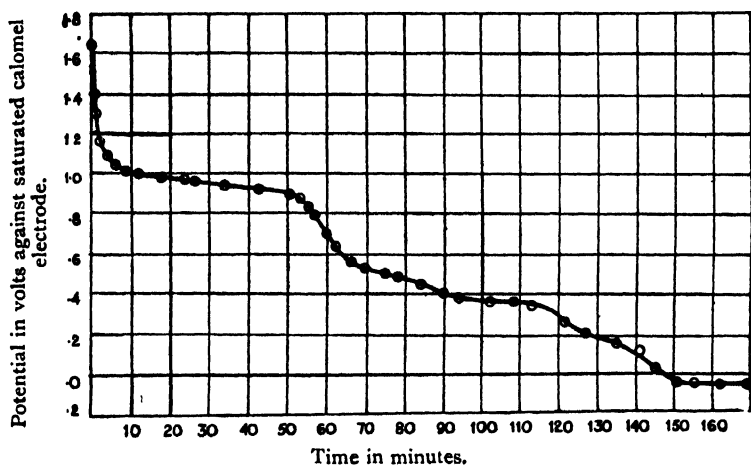


FIG. 4.

high potential condition and to cause a marked persistence of the back *E.M.F.*

For example, with a current of  $5 \times 10^{-3}$  amps. (area of cathode =  $5$  sq. cm., hence current density =  $1 \times 10^{-3}$  amps./cm.<sup>2</sup>, mass of cathode =  $35$  g.), the potential at the surface in a few seconds was  $-2.0$  and beneath it  $-1.7$ . After  $30$  seconds the circuit was opened. The back *E.M.F.* at the surface fell rapidly (to  $+0.35$  in  $1$  min.) but within the body of the cathode it decayed slowly from the high value of  $-1.7$ , taking  $10$  minutes to fall from  $-1.7$  to  $-0.4$  volts. Hence the passage of  $5 \times 10^{-3} \times 30 = 15 \times 10^{-2}$  coulombs, enough to deposit at the most  $15 \times 10^{-2} \div 96,500 = 1.5 \times 10^{-6}$  g. equivalents of active material is sufficient to cause a marked persistence of the back *E.M.F.* This small amount is distributed through  $56$  g. of mercury. With smaller currents a longer time is required, *e.g.*, with a current of  $4 \times 10^{-4}$  amps.,  $20$  minutes were required before the potential beneath the surface reached its characteristic high value of  $-1.7$  volts.

### Identification of Impurities.

The cell was set up as before with  $N/1$   $H_2SO_4$  in the anodic beaker and U tube and 100 c.c. of distilled water in the cathodic beaker and the circuit closed. (160 volts across cell, current  $20 \times 10^{-4}$  amps.) Additions were then made of small quantities (approx. 0.1 g.) of metallic salts of the negative metals starting with sodium, the cell being cleaned and refilled after each addition. The effect in each case was similar. An increase in the polarising current occurred and the cathode attained a characteristic potential for each metal. On opening the circuit the potential fell slowly with time, the decay being more rapid at the surface than it is in the interior of the cathode. The less negative the metal the greater the increase in the

Fall of potential on O.C.  
Potential during electrolysis  
approx. - 2.2 volts.

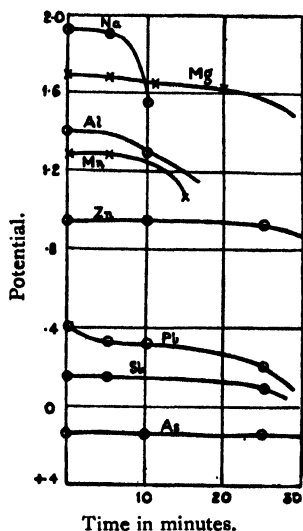


FIG. 5.

impurity with potential of - 0.95 is possibly zinc as this is used in the manufacture of many glasses. It may be noted that when silica vessels were used no flattening was observed at this - 0.95 (zinc) potential. It should be realised that the quantity of impurity necessary to give rise to the observed phenomena is very small, being less than  $10^{-6}$  gm. equivalents.

**Analysis of Solutions.**—The  $N/1$   $H_2SO_4$  was analysed<sup>11</sup> for Na, Mg, Al, Zn, Pb, As, in an attempt to determine if those suspected impurities were present in detectable amounts.

Na, Mg, Al and Zn could not be detected, but a trace of Pb ( $10^{-6}$  g. in 100 c.c.) and arsenic ( $10^{-8}$  g. in 100 c.c.) were found. The same

<sup>10</sup> In "pure" solutions when the high potential condition sets in the potential beneath the cathode surface (or the potential at the surface immediately the circuit is opened) usually has this value of - 1.7 volts, but this is not invariably the case. Occasionally it is - 1.9 volts, or - 1.4 volts. Fig. 6 would identify these impurities as Na and Al respectively. These three Na, Mg and Al could all come into solution from the glass beakers.

<sup>11</sup> For the analysis of these solutions I am indebted to Mr. R. S. Russell, B.Sc.

solution was subjected to prolonged electrolysis (current of .2 amps. for 240 hours) to allow the impurities to accumulate and after the cathode had been left on open circuit for a considerable time, the solution in the cathode beaker was again analysed. Na was now present, Mg, Al, Zn could not be detected. Pb was still present, while the As had increased to  $10^{-6}$  g./100 c.c. In the small volume of solution available, the reactions for Mg, Al, Zn were not sufficiently sensitive to detect quantities of the order of  $10^{-6}$  g. It is significant that when the sensitivity of the reaction is such that quantities of the order of  $10^{-6}$  g. per 100 c.c. can be detected, the suspected impurity is found; also that Na, which is the one alkali metal capable of detection, has appeared, the most probable source being the glass vessels.

### Experiments in Carefully Purified Solutions.

An attempt was made to prepare solutions in which these small traces of impurities would not be present.

(a) Waxed apparatus. Both the acid and the water used in making the  $N/1$   $H_2SO_4$  electrolyte were redistilled in a silica still and the beakers and U tube of the cell were coated with distilled paraffin wax. The cell was set up as a "dilute layer" cell, the electrolyte in the cathodic beaker being approximately  $N/1000$ . On passage of current the high potential condition set in immediately. On open circuit the decay was more rapid than that usually observed, the potential falling from  $-1.7$  to  $+0.1$  in 15 minutes. No flattening could be detected at the Zn and Pb potential, indicating that these metals had been eliminated. That due to As was still present. Owing to its volatility As cannot be completely removed from sulphuric acid by distillation.

After this experiment it was noticed that a small patch of wax had been removed from the glass in the U tube.

(b) Silica apparatus. To obtain a still more pure solution, B.D.H. "As free" sulphuric was twice redistilled in silica. The distilled water also was again twice redistilled in silica. The cell in this case was of silica throughout, and carefully cleaned. It was set up as before, with dilute acid ( $\rho_{H_4}$ ) in the cathodic compartment. On the passage of current the high potential condition did not set in, even after prolonged electrolysis, the potential remaining at  $-1.3$  volts (current of  $10^{-3}$  amps. for 18 hours). On open circuit the decay of potential of the surface was more rapid still, falling from  $-1.3$  to  $+0.2$  in 15 seconds. Beneath the surface also the decay was much more rapid than ordinarily observed, falling from  $-.9$  to  $+0.1$  in 6 minutes. The potential paused at  $+0.1$  to  $+0.2$  for some time before falling to that characteristic of mercury ( $+0.4$ ) indicating that a trace of As is present.

So that with solutions which are very carefully purified and protected from contamination due to the glass of the containing vessels, the persistence of back *E.M.F.* still occurs but is very greatly diminished. Apparently impurities are present in sufficient quantity to influence the fall of potential even when these precautions are taken.

### Persistence of Potential at Other Metallic Cathodes.

In order to determine if the persistence of back *E.M.F.* occurred at cathodes other than mercury, a lead cathode, 5 sq. cm. area was electrolysed in  $N/1$   $H_2SO_4$  with current of 0.4 amps. and the potential measured on open circuit. The characteristic potential of lead in dilute sulphuric acid is  $-0.35$  volt (approx.). The results were as follows:—

Electrolysis at current of 0.4 amps. Potential on closed circuit is - 1.4.

Time of Electrolysis.	Time to Fall on Open Circuit.
5 mins.	To equilibrium value in $\frac{1}{2}$ sec.
25 "	Above - 0.6 for 1 sec.
3 hrs.	" " " 2 "
7 "	" " " 4 "
20 "	" " " 9 "

This shows that a persistence for several seconds does occur at a Pb cathode, the effect increasing with prolonged electrolysis. The cell was then set up with dilute acid ( $N/1000$ ) in the cathodic beaker. After prolonged electrolysis the potential rose to - 1.8 volts and clouds of fine bubbles were evolved, *i.e.*, the cathode was in the high potential condition. On open circuit it now took 4 minutes to fall to the equilibrium value. Silver behaved in a similar manner. Persistence of potential does occur at these cathodes but to a less extent than at mercury. With these solid metals the active material can only accumulate in the surface layers.

### Summary and Conclusion.

After prolonged electrolysis of dilute sulphuric acid the overpotential at a mercury cathode on opening the circuit persists for several hours. This persistence must be due either to active hydrogen or to negative metal impurities. Experimental evidence is advanced to show the latter is the case and these impurities are identified as Na, Mg, Al, Zn, Pb and As. The amount of impurity necessary is very small being less than  $10^{-6}$  g. equivalents. It is shown that the hydrogen ion concentration in the vicinity of the cathode may be very different from that obtaining in the bulk of the electrolyte and that this has an important influence on the rate of fall of the potential. So that even in apparently pure solutions the potential of a cathode on open circuit is controlled by traces of negative metal impurities on its surface. It is apparent that the measurement of these potentials can throw little light on the true hydrogen overpotential. Moreover, since the decay curves are not smooth, measurement of the back *E.M.F.* at set intervals after the circuit is opened and extrapolation to zero time<sup>12</sup> may give a quite erroneous value for the potential at this instant. The presence of these impurities offers a satisfactory explanation of the 'hydrides' observed at a mercury cathode. In general, in order that cathodic back *E.M.F.*'s may be interpreted with confidence as hydrogen overpotential phenomena it is necessary to ensure that metallic impurities of the order of  $< 10^{-6}$  g. equivalents have not been deposited on the cathode surface. Under most experimental conditions impurities are present in amounts greater than this. This also offers a method complementary to that of Heyrovsky,<sup>13</sup> for the detection and identification of traces of impurities in solution.

This problem arose out of previous work done in conjunction with Professor McAulay who, working at the same time but independently in England, arrived at similar conclusions to the above.

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*Note.*—Added by Professor A. L. McAulay.

The object of the present note is to describe two experiments of a different type from the above which by giving negative results help to

<sup>12</sup> Glasstone, *Trans. Far. Soc.*, Mar. 1924.

<sup>13</sup> *Trans. Far. Soc.*, Mar. 1924.

confirm the view put forward that the back *E.M.F.* observed at a mercury cathode showing a hydrogen overpotential is not due to an active form of hydrogen combining with the mercury.

The first experiment consisted in passing the gases from a mercury cathode which showed a high and lasting overpotential over or through a mercury drop arranged by various devices in different pieces of apparatus to be as near as possible to the overpotential cathode. In no case did the mercury drop show any signs of acquiring an overpotential by activation by the gases.

The second experiment had for its object an attempt to produce overpotential artificially by bombarding mercury with monatomic hydrogen. A discharge tube of pyrex had as cathode about 1 c.c. of mercury. Hydrogen at a few cm. pressure was passed through the tube and in some experiments bubbled through, in others passed over the mercury. In every case a heavy condensed discharge from an induction coil was passed through the tube, the red glow of the Balmer series coming well down on the mercury cathode. Great care was taken to keep the cathode cool. The apparatus was so arranged that immediately on stopping the discharge the tube was flooded with  $N/1$   $H_2SO_4$  and the mercury became automatically a half cell completed by a calomel electrode. Although the mercury had been bombarded by monatomic hydrogen in large quantities for about an hour it never became more negative than the calomel electrode.

My best thanks are due to Dr. E. K. Rideal for his encouragement and advice in connection with these and other experiments on similar problems.

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## ON THE NATURE OF THE ACTIVATING RADIATION IN PHOTO-CHEMICAL ACTION.

BY WILFRID TAYLOR, EARL GREY MEMORIAL FELLOW, AND  
ARTHUR ELLIOT.

(Communicated by PROFESSOR G. W. TODD.)

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On previous occasions<sup>1</sup> we have published descriptions of experiments on the rate of combination of hydrogen and chlorine under the influence of white light filtered through chlorine before reaching the mixture. It was shown that the reaction velocity could be measured by a method giving consistent results, and a preliminary study revealed the facts (1) that the actinic power of a beam of light was never totally extinguished by a filter of chlorine as had been previously stated, and (2) that the residual actinic effect of the transmitted light was always much greater than could be accounted for by a strictly exponential law of extinction. The natural conclusion was that the actinic radiations were far from homogeneous, and in the present paper we propose to describe the application of further measurements to an examination of several questions concerning the nature of the radiations absorbed in the process of activation of chlorine.

<sup>1</sup> *Trans. Faraday Soc.*, 23, 31, 1927, and 23, 38, 1927.

### Historical.

Two physical properties of radiation are concerned in photo-chemical action, the frequency and the intensity. According to Draper's Law, the rate of reaction should be proportional to the light intensity for a given frequency, and the law of Grotthus states that only the absorbed frequencies can produce chemical effects. The first of these generalisations was verified by Draper himself, but was refuted later by Baly and Barker,<sup>2</sup> who claimed to have found a wide divergence from strict proportionality, the activity increasing more rapidly than the intensity. Chapman<sup>3</sup> found that Draper's Law was very nearly correct, and this was supported later by the work of Kornfeld and Muller<sup>4</sup> and also by Marshall,<sup>5</sup> but according to Briers, Chapman and Walter,<sup>6</sup> other workers favour a law which expresses the activity as proportional to the square root of the intensity.

Chlorine has two absorption systems at least, details of which have been given by E. R. Laird.<sup>7</sup> There is a general absorption which for a depth of 60 cms. of gas at *N.T.P.* extends from 4650 (all wave-lengths in Angstrom Units) to 2599, and there is also a system of fine structure bands in the visible region, sometimes called the Ribaud bands, but which were discovered by Morren in 1869. They extend from 4799 to 5350; the individual lines do not thicken with increase of gas pressure and, while they undoubtedly contribute to the absorption, there is some doubt whether they are not overlaid by patches of general absorption. Our own experiments deal with the region 3500-6000.

The effect of the frequency finds expression in the relationship between wave-length and Effective Photo-chemical Equivalent, *i.e.* the quantity of absorbing substance removed per unit amount of energy absorbed.<sup>8</sup> (For brevity we shall refer to this simply as the efficiency.) Several workers have considered that two distinct types of absorption exist, one to which we may refer as actinic absorption giving rise to photo-chemical action, and the other producing thermal effects.<sup>9</sup> Recently, some interesting results have been obtained by Lewis and Rideal<sup>10</sup> who found that the Budde Effect shown on illumination of bromine does not appear if the gas be carefully dried, and that the absorption spectra of the two varieties showed corresponding differences. If we assume that in the spectrum of the wet gas, the characteristic absorption of dry bromine is superposed on an actinic absorption band producing the Budde Effect, then reference to the curves of Lewis and Rideal shows (*a*) that only a fraction of the total absorbed energy is used in the activation, and (*b*) the efficiency, as calculated from the total absorption for any given frequency, ought to vary in passing along the band.

Hence both on these grounds and also because of the peculiar double nature of the absorption of chlorine, it is of great interest to investigate the relation of wave-length to efficiency in the case of the hydrogen chloride reaction. An approximate determination of the variation of actinic power (not efficiency) was made by one of us (W. T.),<sup>11</sup> using light filters of fairly

<sup>2</sup> *J. Chem. Soc.*, **119**, 653, 1921.

<sup>3</sup> *Z. physikal. Chem.*, **117**, 242, 1925.

<sup>4</sup> *J. Chem. Soc.*, **129**, 562, 1926.

<sup>5</sup> *Cf. Allmand, Trans. Faraday Soc.*, Feb. 1925, 446.

<sup>6</sup> *Cf. Allmand, Chem. Soc. Reports*, **22**, 338, 1925.

<sup>7</sup> *J. Chem. Soc.*, **128**, 583 and 596, 1926.

<sup>8</sup> *Phil. Mag.*, **49**, 1165, 1925.

<sup>9</sup> *Ibid.*, **125**, 1521, 1924.

<sup>10</sup> *J. physical Chem.*, **29**, 1453, 1925.

<sup>11</sup> *Astrophys. Jour.*, **14**, 1901.

wide spectral range, and measuring the reaction velocities directly. A practical threshold to the actinic region was found about 4900, but the great drawback of the method was that the light intensity within the range of the filter varied greatly. Coehn and Jung<sup>12</sup> also made some measurements by determining the total yield of HCl after long exposures (40 minutes) and fixed a threshold at 5400. Bowen<sup>13</sup> criticised the idea of a real threshold such as is found in the photo-electric effect, and argued that if the figures given for actinic power were used to calculate the efficiency, the latter was approximately constant throughout the actinic region, and hence by extrapolation there would be activation beyond the practical threshold even though the experimental method was insufficiently sensitive to detect it. Furthermore, he concluded that the Ribaud lines were photo-active but the soundness of this deduction appears to us to be doubtful, and allusion to this point will be made again later. Finally a quotation may be made from the paper by Baly and Barker<sup>2</sup>: "There is no doubt that the expansion of the chlorine and its activation is due to the absorption of light of frequencies lying within the ultra-violet absorption band . . . This band must not be in any way confounded with the fine line absorption which extends through the visible region and to which the visible colour of the gas is due."

### Theory of the Method of Integrated Effects.

We now proceed to show how the use of a chlorine filter may assist in clearing up some of the vexed questions detailed above. The experimental arrangement is very simple, and consists of (a) a suitable source of parallel white light having a continuous spectrum without much local variation of intensity, (b) a filter tube in which the concentration of chlorine may be varied, (c) the actinometer, a thin chamber in which the actinic power of the filtered light can be measured by observing the rate of combination of hydrogen and chlorine.

Consider a range of wave-lengths  $d\lambda$  in the original white light, and let the energy density of radiation corresponding to the wave-length  $\lambda$  be  $E_\lambda$  (ergs. per sec. falling normally on unit area). Now let the quantity of energy  $E_\lambda d\lambda$  traverse the column of gas in the filter tube. Its intensity on emerging will be

$$dI_0 = E_\lambda e^{-\alpha \rho l} d\lambda$$

where  $\alpha$  is the molar absorption coefficient for the wave length  $\lambda$ ,  $\rho$  the density of the gas in gram-mols. per litre, and  $l$  the length of the column in cms. The filtered light then falls upon the actinometer and the amount of energy absorbed there is again given by Beer's law as

$$dI = dI_0(1 - e^{-\alpha \rho_2 l_2})$$

where  $\rho_2$  and  $l_2$  refer to the chlorine in the actinometer (the hydrogen being assumed transparent). Hence by summing up all the contributions from the different wave-lengths over a continuous range, we shall obtain the total energy (per sec. per sq. cm.) which is absorbed in the actinometer, namely

$$W = \int E_\lambda e^{-\alpha \rho l} (1 - e^{-\alpha \rho_2 l_2}) d\lambda \quad . \quad . \quad . \quad (1)$$

Turning now to the process of activation, the experiments furnish only a measure of  $K$  the total reaction velocity which includes not only the primary

<sup>12</sup> *Z. physikal. Chem.*, **110**, 705, 1924.

<sup>13</sup> *Phil. Mag.*, **50**, 879, 1925.

reaction but also the secondary processes. It is well known that these multiply the original effect and produce quantum efficiencies ranging up to  $5 \times 10^6$ , but it is usually assumed that the observed reaction velocity is proportional to the rate of activation providing that the sensitivity of the mixture, depending upon the concentrations of water vapour, inhibiting agents, etc., does not change. When the experimental arrangements have been such as to satisfy this condition, then the number of molecules  $k$  reacting per second under monochromatic light depends only on the intensity  $I$ . It is therefore necessary to express the relation between  $k$  and  $I$ , and according to what has been said before, there are three possibilities, namely (1)  $k$  proportional to  $I$  (Draper's Law), (2)  $k$  varying as the square root of  $I$ , or (3)  $k$  involving a positive power of  $I$  greater than unity. Selecting the simplest as well as the best authenticated one, we shall as a first trial regard  $k$  as being directly proportional to  $I$ , and write  $k = cI$ . The next step is to extend  $k$  from the case of monochromatic light to  $K$  the total reaction, and we must here introduce a second assumption by which the efficiency  $\phi$  is related to the wave-length. As before, we shall take the simplest case for the first trial, and assume that  $\phi$  is independent of  $\lambda$ , so that the total reaction velocity becomes  $K = CW$ , where  $C$  is a constant, and  $W$  is given by equation (1). The variables in the final equation will be considered to be  $K$  and  $p$ , and we shall proceed to test our hypotheses by using them to obtain the function  $K = f(p)$  and comparing it with the same function as determined experimentally.

To calculate the values of  $K$ , we require a knowledge of the subsidiary functions  $\alpha = f(\lambda)$  and  $E_\lambda = f(\lambda)$ . The first of these has been carefully determined by von Halban and Siedentopf,<sup>14</sup> and the second entails a measurement of the distribution of spectral energy in the light employed.

### Experimental Work.

The technique of measuring the reaction velocities had already been worked out, and preliminary measurements had been made using (1) a filter tube 45 cm. long, (2) another tube 159.5 cm. long, and (3) a solution of chlorine in carbon tetrachloride. Although these observations all agreed in yielding "residual effects," nevertheless when the various concentrations were reduced to common units, the three curves showed slight differences. More accurate work showed that these differences were due to an inefficient method of filling the long tube with chlorine. The most prolonged gas streaming never removes the air completely, and therefore the filter tube was connected with a well tested vacuum system, and made air-tight to the standard of high-vacuum work. Three alternate sets of evacuations and refills were then sufficient to reduce the air content to quite negligible proportions. The chlorine was obtained from a commercial cylinder, and passed through concentrated sulphuric acid. Pressures were measured on a mercury manometer protected by paraffin, and the reaction velocities determined in the manner described in the earlier papers. The final results are given in the following table and are found to agree very well with those of cases (1) and (3) above, as well as with an independent set in which the Draper expansion had been used to measure the actinic power. The concentrations are given here in terms of the number of molecules in a column of unit cross-section and the same length as the tube, and calculated from the recorded pressures  $p$  after correction for temperature and barometric

<sup>14</sup> *Z. physikal. Chem.*, 103, 71, 1922.

pressure. A large number of similar sets of results were obtained, but to save space, only a typical sample has been given, and it is sufficient to say that all the experimental curves coincided.

TABLE I.  
EXPERIMENTAL DETERMINATION OF THE FUNCTION  $K = f(p)$ .

Chlorine Pressure in Filter, $p$ .	Concentration (Molecules per Sq. Cm. Cross-section,	Relative Reaction Velocity, $K$ .
(cm. Hg.)	$\times 10^{20}$ .	
0	0	1.24
2.2	1.18	0.70
6.1	3.35	0.34
10.7	5.75	0.179
20.4	10.96	0.079
35.2	18.91	0.050
75.1	40.34	0.029
56.1	30.14	0.041
9.9	5.32	0.219

The distribution of energy in the illumination was next determined by one of us (A.E.). The source of light was a 100 c.p. "Ediswan Pointolite," and this being a tungsten arc in addition to an incandescent electrode could not be assumed to be amenable to treatment based on the radiation laws. The light from both arc and electrode together was examined with a spectrograph, and as the arc lines were found to be superposed upon the continuous background, it was decided to make a direct determination of the energy distribution with a thermopile. The same optical train of lenses as employed in the photo-chemical work was of course retained; the limit of absorption of the glass in this train was approximately 3500, and from the photographs, the arc lines in the transmitted region were found to be feeble compared with the radiation from the electrode except very near the absorption limit.

The thermopile used was a linear one consisting of fifteen copper-constantan couples made after the manner described by Moll<sup>15</sup> each of 1 cm. length and 0.002 cm. thickness, soldered on copper pins mounted in ebonite. The thermopile was mounted in a tube fitting the spectroscope, and was provided with a fixed slit of 2 mm. width. It was found to be very sensitive and quick in response, but required very careful shielding to prevent temperature variations in the room from causing drift of the galvanometer indicator. The galvanometer used was a Coblenz astatic instrument of 10 ohms resistance. When used at the high degree of sensitivity necessary (approximately 1 mm. per  $10^{-10}$  amp.) it is essential to use massive magnetic shields, and three concentric sets of "Stalloy" rings were employed. In spite of the screening, work could only be carried out between 1 a.m. and 6 a.m., the galvanometer being then perfectly steady.

As the energy radiated in the violet and ultra-violet by a 100 c.p. Pointolite is very small, it was necessary to use a large aperture spectrometer (40 mm.) and a slit of 1 mm., the image of the electrode being thrown on the slit by a large condenser.

The deflections corresponding to various wave-lengths from the limit of

<sup>15</sup> *Proc. Physical Soc.*, 35, 257, 1922.

transmission at 3500 to 5000 were determined with this system and the readings continued to the red end of the spectrum with a less sensitive galvanometer, but only the former were actually required. A curve was then drawn giving the readings plotted against wave-length, but the curve so obtained was not the true energy curve of the light, but had to be corrected for the variation in the dispersive power of the glass prism. The actual galvanometer deflections  $D$  were multiplied by  $ds/d\lambda$ ,  $s$  being the scale reading of the spectrometer, according to the theory given in works on optics. The values of  $ds/d\lambda$  given in Table II. were obtained by drawing a large scale calibration curve of  $s$  and  $\lambda$ , and then estimating the tangents.

TABLE II.

DISTRIBUTION OF ENERGY IN THE SPECTRUM OF THE WHITE LIGHT USED IN THE PHOTOCHEMICAL EXPERIMENTS.

The Function  $E_\lambda = f(\lambda)$ .

Wave Length Angström Units.	$ds/d\lambda$ .	Relative Galvanometer Deflection, D.	Corrected Energy, $E_\lambda$ .
		(cm.)	
3700	1.50	0.1	0.15
3800	1.40	0.25	0.55
4000	1.20	0.65	0.78
4200	1.01	1.2	1.21
4400	0.83	2.1	1.74
4600	0.69	4.0	2.76
4800	0.59	6.6	3.89
5000	0.53	9.7	5.14
5500	0.40	21.1	8.44
6000	0.29	37.3	10.82

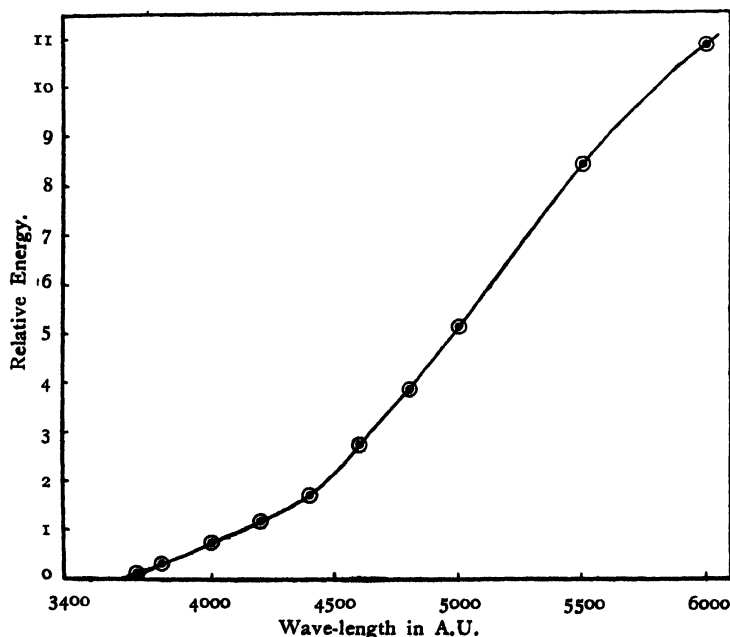


FIG. 1.—Energy distribution in spectrum of Pointolite lamp (the function  $E_\lambda = f(\lambda)$ ).

### Analysis of the Results.

Since the integral in equation (1) contains two arbitrary functions, the evaluation must be carried out by graphical methods. The functions in question,  $a = f(\lambda)$  and  $E_\lambda = f(\lambda)$  were drawn on a large scale on squared paper, and values deduced by interpolation at suitable points. Since the integral may be written as

$$W = \int \psi e^{-a\rho l} d\lambda$$

where

$$\psi = E_\lambda(1 - e^{-a\rho l_2})$$

the values of  $\psi$  were calculated first for representative wave lengths  $\lambda$ . Values were then selected for  $\rho$  and corresponding to each, the magnitude of  $Z = \psi e^{-a\rho l}$  was obtained. A graph was then drawn of the function

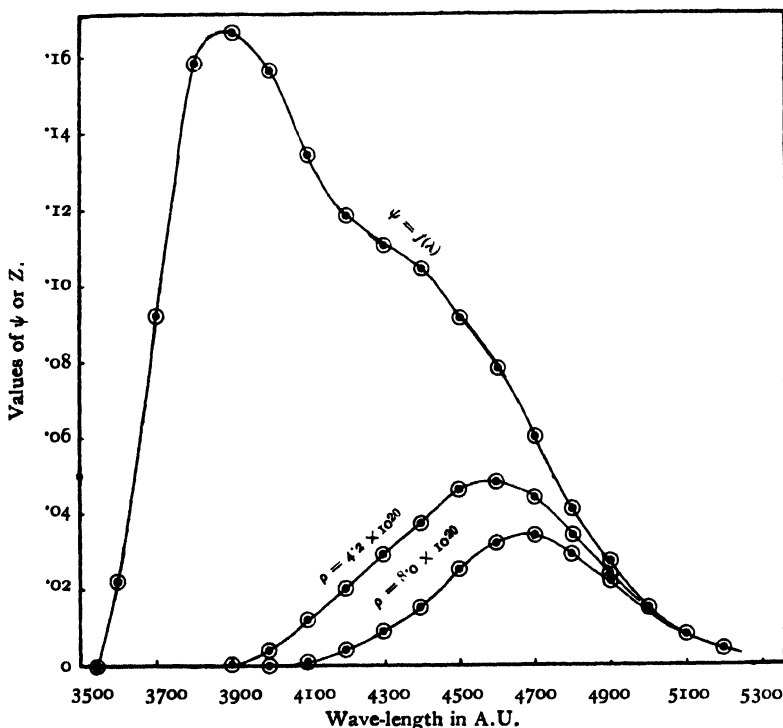


FIG. 2.—The functions  $Z = f(\lambda)$  for  $\rho = 4.2 \times 10^{20}$  and  $8.0 \times 10^{20}$ , and the function  $\psi = f(\lambda)$ .

$Z = f(\lambda)$  in each case, and the area under each curve taken as the value of the integral  $W$ . In this way a set of corresponding values of the variables  $W$  and  $\rho$  were obtained, and the function graphed. These calculations are summarised in Table III, the remaining data being given below:—

Mean depth of actinometer cell = 2 cm.

Concentration  $\rho_2$  in actinometer = 0.0207 g. mols per litre.

Length of filter tube = 159.5 cm.

Factor to convert N molecules per sq. cm. cross-section into g. mols per litre =  $1.034 \times 10^{-23}$ .

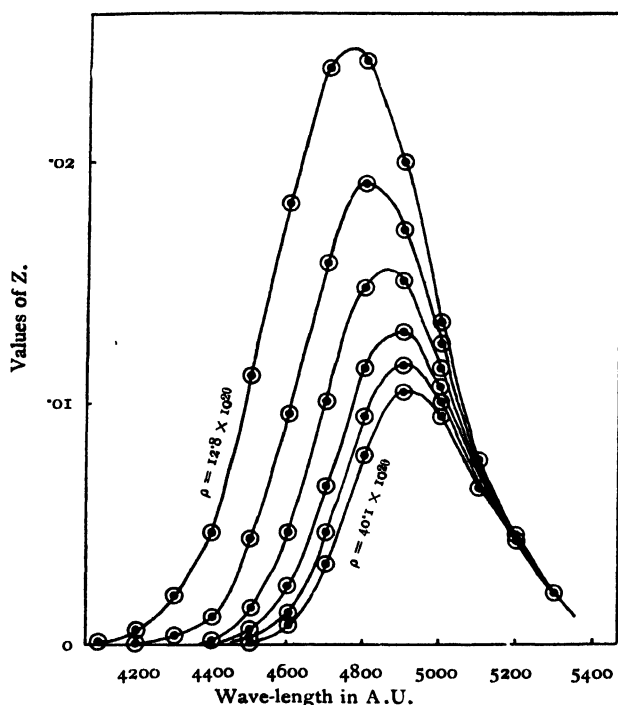


FIG. 3.—Graphs of function  $Z = f(\lambda)$  for values of  $\rho = 12.8 \times 10^{20} - 40.1 \times 10^{20}$ . (See Table III.)

TABLE III.

CALCULATION OF THE FUNCTION  $W = f(\lambda)$ .

1.	2.	3.	4.	5.								
$\lambda$ .	$E_{\lambda}$ .	$\text{Log } a$ .	$\psi$ .	4.2	8.0	12.8.	18.5.	24.8.	30.9.	35.7.	40.1	
3500	0	1.66	—									
3600	0.03	1.52	.0224									
3700	0.15	1.36	.0919									
3800	0.35	1.16	.1577									
3900	0.57	0.93	.1662	.0005								
4000	0.80	0.72	.1563	.0040	.0002							
4100	1.00	0.54	.1337	.0120	.0014	.0001						
4200	1.20	0.40	.1186	.1204	.0044	.0006	.0001					
4300	1.45	0.28	.1101	.0293	.0091	.0020	.0003					
4400	1.75	0.17	.1040	.0373	.0150	.0046	.0011	.0002	.0001			
4500	2.25	0.00	.0913	.0457	.0247	.0111	.0043	.0015	.0006	.0003	.0001	
4600	2.75	9.84	.0781	.0484	.0316	.0182	.0095	.0046	.0023	.0013	.0008	
4700	3.30	9.64	.0597	.0442	.0337	.0238	.0158	.0100	.0055	.0046	.0033	
4800	3.9	9.40	.0410	.0344	.0294	.0241	.0190	.0147	.0114	.0094	.0078	
4900	4.5	9.16	.0270	.0244	.0223	.0199	.0155	.0150	.0129	.0115	.0104	
5000	5.2	8.88	.0516	.0148	.0141	.0133	.0124	.0114	.0106	.0100	.0088	
5100	5.8	8.53	.0081	.0079	.0078	.0076	.0073	.0071	.0068	.0066	.0065	
5200	6.5	8.20	.0046	.0045	.0045	.0045	.0044	.0044	.0044	.0043	.0043	
5300	7.2	7.80	.0007	.0007	.0007	.0007	.0007	.0007	.0007	.0007	.0007	
				67.3	15.78	9.79	6.45	3.87	3.44	2.77	2.21	2.12
				1.24	.231	.143	.094	.057	.050	.041	.032	.031

The areas under the  $Z/\lambda$  curves are given at the foot of each column, and beneath them, their relative values when reduced so as to make the white light value 1.24. (The theoretical activation for white light is of course obtained from the  $\psi - \lambda$  curve itself.) The figures at the heads of the columns are the concentrations  $N$ , and should be multiplied by  $10^{20}$ .

The theoretical points from Table III. as well as the actual experimental points from Table I. are plotted in Fig. 4. Having consideration of the

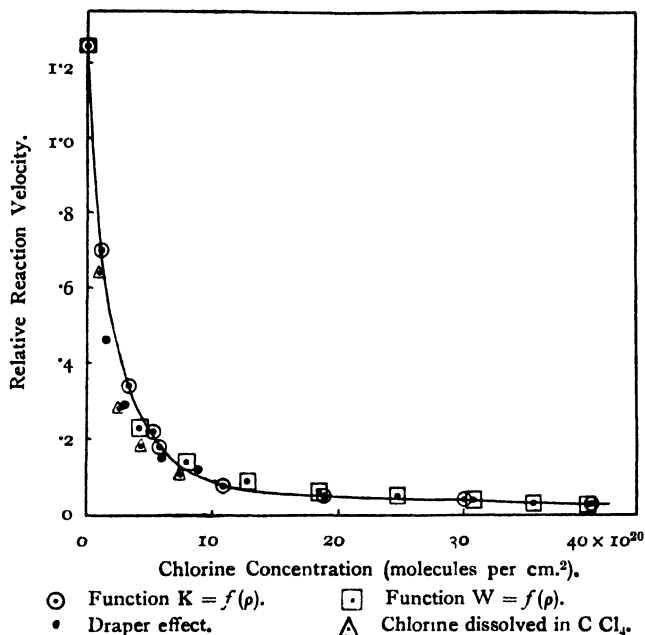


FIG. 4.

limits of accuracy involved, we are not entitled to draw more than one curve through all the points, and it will be seen from the figure that they all lie very close to the single line. In order to stress the reliability of the experimental results, some points have been added which are derived from the results given in previous papers, and including some for which the light was filtered through chlorine dissolved in carbon tetrachloride. In estimating the degree of accuracy, it must be remembered that all the final values involve graphical estimation of tangents to curves.

### Conclusions.

The very close agreement of the functions  $W$  and  $K$  enables us to draw very clear deductions upon the questions under consideration. Our results may be presented briefly as follows:—

It has been found impossible to distinguish within the limits of error any difference between the experimental results and those calculated on the assumptions:

(a) That the efficiency is independent of the frequency throughout the range 3500–5500.

(b) That for a given frequency the activation is directly proportional to the light intensity.

Hence there is no evidence that we are dealing with two different types of absorption, "actinic" and "thermal." It is evident that the activation is due to the whole of the general absorption band of chlorine itself, and not to highly efficient superposed bands. This may account for the failure of the attempt to separate the isotopes of chlorine by photo-chemical methods, since the general absorption is continuous even in the highest resolving powers. Furthermore we have shown that the chlorine molecule absorbs just the same actinic radiation when it is in the gaseous state, as when it is dissolved in carbon tetrachloride.

From an inspection of Table III., it may be seen that the most feebly absorbed radiations have their maximum actinic effect at 4900, which is where the "practical threshold" would be fixed by any method not capable of great delicacy, whereas the limit at which the activation becomes infinitesimal is 5400, this being just where Coehn and Jung were able to detect the last traces of HCl formation in their prolonged exposures.

We must admit that the evidence is insufficient to assign photo-activity to the Morren or Ribaud lines. We deduce from the data of Laird that for a tube of chlorine at *N.T.P.* 150 cm. long the limit of the continuous absorption is 4850, and hence activation is to be accounted for in the region from there to 5400. The Morren lines occupy 4800-5350, but it is just here that Laird describes the spectrum as having a fluted appearance, and says: "it is possible that this . . . may be due to narrow patches of general absorption superposed on the line spectrum." We have no means of knowing how the absorbed energy is distributed, and therefore until more information is forthcoming about the absorption of chlorine in the region 4850-5350, this interesting problem must be left unsolved.

Finally it may be stated explicitly that the effect of the variation in the size of the quantum with wave-length has not been considered, and neither has the conception of the quantum efficiency been introduced. It has only been intended to show that the experimental results are capable of interpretation by making two very simple assumptions relating to the effective photo-chemical equivalent.

### Abstract.

Actinic extinction curves have been obtained by allowing light filtered through various concentrations of chlorine to activate a mixture of hydrogen and chlorine. The activating radiation is shown to be non-homogeneous, and it is shown that the experimental results can be accounted for to a high degree of approximation by assuming (1) that the effective photo-chemical equivalent of monochromatic light is independent of wave-length between 3500 and 6000, and (2) that for a given frequency the actinic power is directly proportional to the intensity.

No evidence is found for assuming that any part of the ordinary optical absorption in this region has special chemical properties, or that two different types of absorption actinic and non-actinic are superposed.

We desire to record our gratitude to Dr. G. W. Todd and Dr. W. E. Curtis for the facilities placed at our disposal as well as for their helpful advice throughout.

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# THE EFFECT OF SERIES RESISTANCE ON THE CURRENT FROM A PHOTO-ACTIVE CELL CONTAINING A FLUORESCENT ELECTROLYTE.

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A peculiar property which has been attributed to the photo-active electrolytic cell, composed of a fluorescent electrolyte and platinum electrodes, is the independence of the current with respect to the external resistance of the circuit. It was first described by Goldmann<sup>1</sup> who obtained nearly identical curves for the growth of the current produced by illumination with an external resistance of 103,000 ohms and with one of 3000 ohms. One of the authors<sup>2</sup> obtained similar results, introducing into the circuit resistances up to one megohm. It was observed, at that time, that when the current had reached a steady value, if the external resistance was changed keeping the illumination constant, the current measuring instrument gave a sudden throw and then returned to approximately the original reading. There was also found a similar effect when the cell was not illuminated, but was producing a small current due to dissimilarities of the electrodes. This seems to suggest that the apparent invariance of the current is associated with the electro-chemical properties of the cell rather than with the photo-active properties. In fact, the behaviour of the current is very similar to that observed when an electrolytic cell is polarised by a small impressed electromotive force. If the current is independent of the resistance, it can be so for only a limited range since, if the current remains constant while progressively larger values of resistance are used, a point will be reached at which the heat developed in the resistance will equal the maximum power available. At this point, then, if not before, the value of the current must decrease with further increase of resistance.

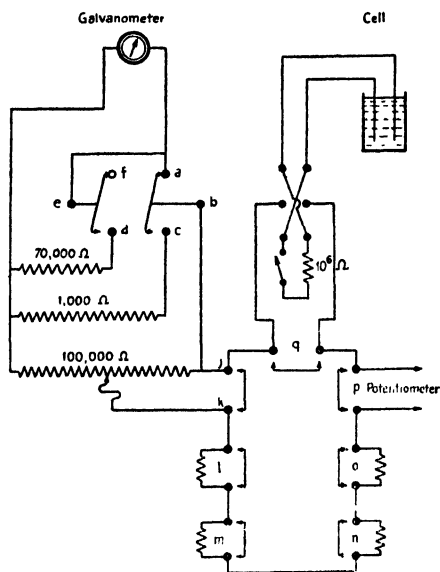


FIG. 1.

<sup>1</sup> Goldmann, *Ann. Physik*, **27**, 449 (1908).

<sup>2</sup> Murdock, C. C., *Physical Rev.*, **17**, 626 (1921).

This investigation was started to find such an upper limit to the invariance of the current. Radio grid leaks were used for the values of the resistance up to 25 megohms, and pencil marks on paper for values up to 75 megohms. As these resistances cannot be relied upon to remain constant, the apparatus was so planned that their values could be measured during the progress of an experiment. Fig. 1 is a diagram of the electrical connections. Seven pairs of mercury cups are connected in series. One pair, *g*, is connected through a reversing switch to the electrolytic cell. Cups *j* and *k* are connected through a 100,000 ohm Ayrton universal shunt and a rocker switch to a D'Arsonval galvanometer. To *l* is connected a standard megohm; to *p*, a low resistance potentiometer for introducing into the circuit known electromotive forces; and to *m*, *n* and *o*, may be connected various resistances as desired.

Because of the length of time required for the cell to come to a steady state after any considerable alteration of the circuit, it was found desirable to keep the cell always on closed circuit during the period of investigation. The circuit is so arranged that changes can be made in any part of it, without disturbing the cell, by short circuiting the appropriate mercury cups. The megohm at the reversing switch can be shunted across the cell when that switch is to be opened. The galvanometer has an internal resistance of 1000 ohms and gives a scale deflection of 6.8 mm. per  $10^{-10}$  amperes. It was necessary to make frequent observations of the zero reading. This can be done by throwing the rocker switch to position, *d c*, which substitutes the 1000 ohm resistance, shown in the diagram, for the galvanometer in the cell circuit and connects a 70,000 ohm resistance across the galvanometer terminals. With this resistance the galvanometer is critically damped and a zero reading can be quickly made. The cell is now in a circuit having the same resistance as before and the process of its approach to a steady state condition is not interrupted. The levels of the mercury in the cups of the rocker switch are so adjusted that, while the switch is being thrown to position, *d c*, the operations occur in the following order: the 1000 ohm resistance is shunted across the galvanometer, the galvanometer is disconnected and, finally, the 70,000 ohm resistance is connected to the galvanometer. Thus, throwing the switch in either direction, only disturbs the cell by reducing the resistance of its circuit by 500 ohms for the fraction of a second that the 1000 ohm resistance and the galvanometer are connected in parallel.

Alcoholic solutions of rhodamine-B ranging in concentration from 0.3 per cent. to 6 per cent., have been used as electrolytes and for electrodes both bulk platinum and transparent platinum films on glass. We find that the introduction of resistance into the circuit always decreases the value of the steady state current. For the range of resistances used the reciprocal of the current can be represented as a linear function of the resistance within the limits of experimental error. This law has been found to hold when the current is produced by illumination or when produced by a small electromotive force, either internal or external. Line A of Fig. 3 illustrates the case of a current produced by illumination. Here, the reciprocal of the current in  $10^{-10}$  amperes is plotted against the external resistance in megohms. The  $x$ -intercept obtained in these experiments is always much larger than the internal resistance of the cell as measured by an impedance bridge. The cells used had resistances of the order of 0.01 megohms, while the values of the negative  $x$ -intercepts in the various experiments range from 0.5 to 12 megohms. These values are

also large in comparison with the values of the external resistances that have usually been employed in testing the law of invariance of the current.

The results can be expressed by the equation:

$$1/i = S(r + R) \quad (1)$$

in which  $i$  is the current;  $r$ , the resistance of the circuit;  $S$ , the slope of the experimental line; and  $R$ , its negative  $x$ -intercept diminished by the resistance of the shunted galvanometer and that of the cell. This correction is in most cases much less than the uncertainty in the value of  $R$ .

From equation (1) we obtain for the total electromotive force of the circuit:

$$ri = 1/S - Ri \quad (2)$$

Thus, the results of experiment indicate that the electromotive force of the circuit is comprised of a part measured by  $1/S$  which is independent of the current and a negative part,  $-Ri$ , proportional to the current.

The throw observed when the resistance of the circuit is changed in the case of either the photo-current or the dark current is suggestive of that obtained when a small impressed electromotive force is applied to a cell. This latter effect finds explanation in the fact that the cell is polarised by the products of electro-chemical decomposition. The throw is produced by the passage of the electricity necessary to bring about the polarisation of the cell. Various agents such as diffusion and convection tend to depolarise the cell by removing the polarising material from the electrodes. When after the throw a steady current is attained, the value of it is such that it brings polarising material to the electrodes at the same rate as that at which the depolarising agencies remove it. This current, called the residual current, is thus proportional to the rate of dissipation of the polarising material. In this steady state, the counter-electromotive force of polarisation is less than the impressed electromotive force by an amount  $ri$ , where  $r$  is the resistance of the circuit and  $i$ , the residual current.

There seems to be no reason why small electromotive forces inside the cell due to dissimilarities in the surface of the electrodes or to an asymmetrical concentration distribution in the electrolyte should not bring about steady state conditions similar to those produced by an external electromotive force, provided the electromotive force finds its cause in an agency which is independent of the state of polarisation of the cell. If, under these conditions, we change the value of the resistance, we at once change the current and this, in turn, begins to affect the polarisation. The current and the polarisation continue to react mutually upon each other until a steady state is set up in which material is brought to the electrodes by the current at the same rate as that at which it is dissipated by the depolarising agencies.

According to this view, the photo-current in its steady state, is simply the residual current resulting from an electromotive force produced by illumination and the term  $Ri$  of equation (2) is due, in part at least, to the polarisation. If this is the case anything which tends to facilitate depolarisation should decrease the value of the coefficient  $R$ . This may be accomplished by stirring the solution, thus making more easy the passage of the polarising material from the electrodes.

For this purpose, a vessel containing the solution was placed on a table capable of being rapidly rotated by an electric motor and the electrodes were mounted on a stationary support so as to dip into the solution. The electrodes were similar to those recently used in an investigation of

the location of the electromotive force.<sup>3</sup> They consisted of semi-transparent platinum films, deposited by cathodic sputtering on the outside of a glass test tube, 16 cm. long and 1.8 cm. in external diameter. The electrodes

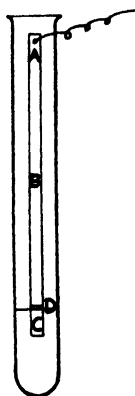


FIG. 2a.

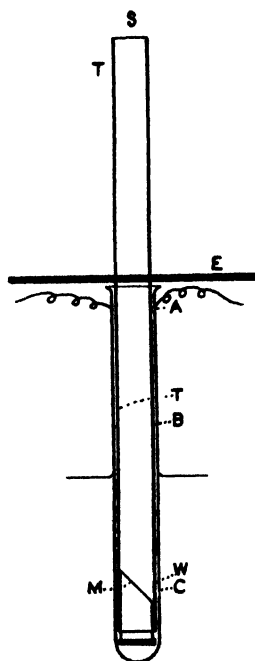


FIG. 2b.

were on the opposite sides of the test tube. One of them is illustrated in Fig. 2a. C is a semi-transparent film, 5 mm. by 15 mm.; B, an opaque platinum film serving as a lead. To B at A is soldered a fine copper wire for making connection to the measuring apparatus. The lead, B, and the upper part of C as far as the line D is insulated from the solution by a thin coat of bakelite lacquer which was baked at a temperature of 140° C. for several hours. The brass tube T (Fig. 2b) is covered by a layer of felt over which the test tube fits snugly. In the wall of the brass tube at W is a rectangular window, 6 mm. by 12 mm. Light from a source, S, is reflected by the mirror, M, through the window and the electrode into the electrolyte. The lower limit of the insulation, D, is below the upper edge of the window so that the part of the semi-transparent film C, which is in contact with the solution is completely bathed in light. By means of a lever attached to its upper end, the test tube can be rotated so that the electrode C is at one side or the other of the window and thus in darkness except for fluorescent and scattered light from the illuminated solution. The circular disk, E, carries a scale for reading the position of this lever and also serves to screen the solution from direct illumination by the source S. The source of light, a 100 watt concentrated filament lamp, is clamped rigidly to the upper part of the brass tube. The whole unit forms a pair of dipping electrodes, very convenient for comparing the photo-active properties of solutions.

When this tube is mounted with its axis nearly coincident with the axis of rotation, rapid motion of the table produces turbulent motion of the fluid and at the same time tends to carry it from the neighbourhood of one electrode to that of the other. There results an efficient stirring of the solution. The effect of stirring the electrolyte has been investigated for both the dark current and the photo-current. It was found that stirring decreased the value of the photo-current and increased that of the dark current. Fig. 3 represents the case of the photo-current. The electrolyte

was a 3 per cent. solution of rhodamine-B in alcohol. The data taken when the solution was at rest is plotted in line A and that taken with rotation at 80 revolutions per minute in B. Lines A and B, Fig. 4, show similar results with the same cell and solution taken a few days later. The speed in this case was 95 revolutions per minute.

<sup>3</sup> Murdock, C. C., *Proc. Nat. Acad. Sci.*, 12, 504 (1926).

In taking the data for Fig. 3, particular care was taken to avoid errors due to slow changes in the condition of the cell. The data were taken in sets alternately at rest and in motion, each set consisting of several data at a variety of resistances. Each point of the lines A and B represents an average of the values from all the sets for the resistance concerned. The deviations of the individual points from the lines A and B are shown to larger scale at A' and B'. The condition of the cell remained very constant during this experiment and no systematic variation with time was observed.

The method of taking the data for B, Fig. 4, was such as to give a measure of the effect of changing the speed of rotation. At each value of the resistance data was taken alternately at 95 and 156 revolutions per minute until the change in the current produced by the change in speed was definitely established. The values of the current at the two speeds are

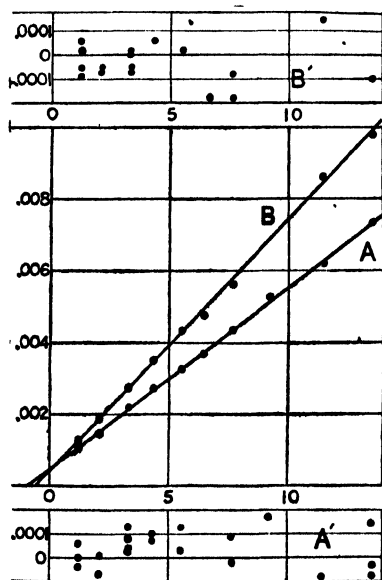


FIG. 3.

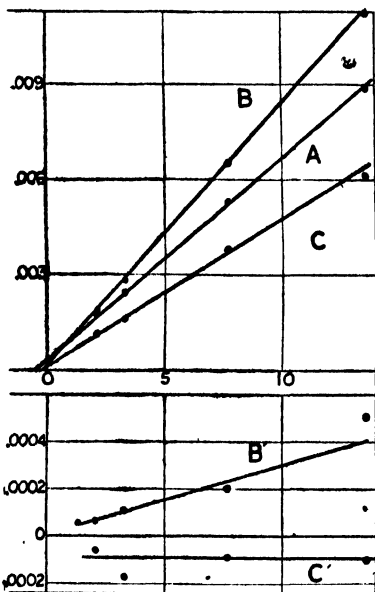


FIG. 4.

nearly equal, but the current is always less at the higher speed. B', Fig. 4, shows the change in the reciprocal of the current produced by the increase of speed.

The effect of stirring is seen to be twofold, a decrease in the intercept and an increase in the slope, causing the lines for rest and motion to cross near the  $y$ -axis. We have found no exceptions to this behaviour. The decrease in the intercept is the result to be expected if the intercept is due to polarisation. The increase in the slope signifies a decrease in the value of the electromotive force. In Fig. 3, the change is from 0.195 to 0.145 volts; in Fig. 4, from 0.155 to 0.115 volts. It is of interest to note that while the electromotive force is different in the two experiments due to a loss in the sensitivity of the cell in the interim the ratio of the electromotive force in motion to that at rest is practically 0.75 in both experiments.

Grumbach<sup>4</sup> has shown that in the case of dilute solutions of uranine in

<sup>4</sup>Grumbach, *Comptes Rendus*, 176, 88 and 177, 395 (1923).

water with an excess of sodium hydroxide, the photo-electromotive force consists of two electromotive forces; one,  $E_p$ , due to the illumination of the surface of the electrode and the other,  $E_c$ , due to a change in the electrolyte produced by illumination. He found in the case of uranine that  $E_p$  was positive and  $E_c$  negative. One of the authors<sup>3</sup> using the apparatus described in this article has shown that the photo-electromotive force in the case of a 3 per cent. alcoholic solution of rhodamine-B is due in part, at least, to changes in the electrolyte produced by illumination. In this case  $E_p$  is positive. There is some indication that  $E_c$ , if present, is also positive.  $E_p$  seems to be due to the difference in the concentration at the two electrodes of a product which results from the illumination of the electrolyte. Stirring the solution would tend to decrease this difference in concentration and consequently produce the decrease in the electromotive force observed.

The effect of increasing the speed of rotation shown in B' of Fig. 4 is so small that the resulting changes in the current are of the same order of magnitude as the errors of observation. The points, however, lie so as to clearly indicate a positive slope for the line B'. The line as drawn corresponds to a decrease in the electromotive force of about 0.004 volts. A 64 per cent. increase in the speed of rotation has produced a 3.5 per cent. decrease in electromotive force. It seems from this that at these speeds nearly all the variation in the electromotive force which can be expected from stirring is obtained. This may mean that we have nearly reduced  $E_p$  to zero and that the remaining electromotive force is a measure of  $E_c$ . It seems more likely, however, that with light streaming through the electrode and producing its maximum effect upon the solution close to the surface of the electrode, there would be a part of  $E_p$  which could not be eliminated by stirring. This part of  $E_p$  is not easily distinguished from a possible  $E_c$ , when a highly absorptive solution is illuminated through the electrode.

Experiments have also been performed with a uranine solution made by dissolving 0.5 g. of fluorescein in an eighth normal aqueous solution of sodium hydroxide. The electromotive force was found to be negative and stirring by rotation at 190 R.P.M. changed its value from -0.065 to -0.01 volts. This is a much larger relative change than was obtained with rhodamine-B. It is in general agreement with the results of Grumbach,<sup>4</sup> if, as seems probable, the stirring is only partially effective in eliminating the electromotive force due to the effect of illumination on the electrolyte. If this is so, then, the result of stirring is to diminish the numerical value of the negative  $E_c$  until it is only slightly greater than the positive  $E_p$ , giving a small negative total electromotive force. In the case of rhodamine-B with both  $E_p$  and  $E_c$  probably positive, a similar fractional change in  $E_p$  would produce a smaller fractional change in the total electromotive force as observed.

In order to make a direct comparison between the photo-current and the residual current, observations were taken when the cell was not illuminated, the current being produced by an external electromotive force of 125 volts. This data is shown by C and C', Fig. 4, and was taken in the same manner as that shown in B and B'. In this case the speeds of rotation were 100 and 170 R.P.M. The ordinates of C' are all negative and there is no definite indication of either a positive or a negative slope. The increase in speed tends, therefore, to displace the line C to a parallel position. No change in the electromotive force of the circuit is indicated, the increase in the current being associated with a decrease in R. This is the result which the theory of the residual current would lead us to expect. Similar behaviour is observed in the case of the dark current. The electromotive

force of the electrodes used for the experiments of Figs. 3 and 4 was too small for accurate measurements of the dark current. Observations were made with a similar pair which gave  $R = 4.5$  megohms and  $1/S = 0.040$  volts. The following are the values of the changes in the reciprocals of the current produced by rotation:—

Resistance	0.5,	1.0,	1.7,	2.2
$\Delta(1/i)$	- 0.0012,	- 0.0010,	- 0.0014,	- 0.0013

Since these values are the same within the errors of observation, no change in the electromotive force is indicated.

Swensson<sup>5</sup> has suggested an explanation for the constancy of the photo-current based upon a theory which he developed to explain the results of his experiments on the illumination of inorganic electrolytes by ultra-violet light. He makes the following assumptions: (a) the light changes the molecules of the electrolyte from their original form, B, to another form, A, at a rate proportional to the light intensity and to the concentration; (b) the form, A, spontaneously goes back to form B at a rate proportional to its concentration; (c) the passage of the current removes form B from the solution at a rate proportional to the current; (d) the electromotive force is that due to the concentration of form A.

Swensson develops the theory for a variety of cases, including that in which the light is totally absorbed and the solution stirred so that the concentration of form B is uniform in the region of the illuminated electrode. For this case, he obtains an expression agreeing in form with our experimental equation (1). In his nomenclature the coefficient,

$$R = \frac{k_2 \rho}{k_1} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which  $k_2$  is the rate of removal of form A per unit of current;  $\rho$ , the electromotive force per unit difference in concentration of form A at the surfaces of the electrodes; and  $k_1$ , the rate of spontaneous disappearance of form A per unit concentration. He points out that if  $k_1$  is small, the effective value of  $R$  will be large and for small changes in the external resistance the value of the current will seem to be invariant.

The fundamental assumptions of Swensson are in no way inconsistent with the views expressed above. In fact they are essentially the same as those made to account for the part,  $E_w$ , of the electromotive force produced by illumination. No account is, however, taken of polarisation. That this is present even with the most thorough stirring is shown by the fact that upon changing the resistance a throw of the galvanometer always occurs. The intercept,  $R$ , seems to be the same within the accuracy of its determination for the photo-current and the dark current. Thus it seems that polarisation is sufficient to account for the results and that the effect due to the possible spontaneous transformation of the form A to the form B is relatively small. The theory of the residual current gives an expression for  $R$  very similar in form to that given by Swensson's theory, namely:—

$$R = \frac{f \rho}{k} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here  $\rho$  is the same as in equation (3) but relates to the polarising material;  $f$  is the rate at which this material is transferred by a unit current, and  $k$  the rate at which it is dissipated from the electrodes per unit difference in its

<sup>5</sup> Swensson, *Ark. f. Kem., Min. och Geol.*, 7, 1 (1919).

concentration. It is interesting to note that in both theories a large value of  $R$  is explained by a small rate of disappearance of material per unit concentration. In equation (3) the disappearance is a transformation into another form, and in equation (4) a transference through the solution.

We have found no evidence of a systematic deviation from the law of equation (1) at either limit of the range of resistances investigated. For this range then,  $R$  is independent of the current. This is explained if the coefficients  $\rho$ ,  $f$  and  $k$  of equation (4) are all independent of the degree of polarisation. In general this is not the case, but it may be approximately true for small polarisations.

The theory of the residual current has been quantitatively verified by Cottrell<sup>6</sup> for the case in which the diffusion of the ions of the metal constituting the electrodes was the only depolarising agency. In this case,  $\rho$  is an exponential function of the polarisation, approximately constant at low values of the polarisation and proportional to the polarisation at high values. The residual current is independent of the resistance for large values of the polarisation, for from equations (1) and (4) we may write:

$$i = \frac{Kp}{f_0} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $p$ , the polarisation, is written for  $(\frac{1}{S} - r i)$ . If  $\rho$  is proportional to the polarisation,  $i$  becomes independent of it. If the value of  $\rho$  in our cell depended similarly upon the polarisation, we would expect the experimental lines to become concave upward for low resistances and approach parallelism to the  $x$ -axis for small values of  $r$ . No evidence of this has been found, although the largest value of the polarisation observed, 0.085 volts, is considerably greater than that at which the effect appears in a cell of the type used by Cottrell.

An effect of this sort may account for some of the experimental verifications of the invariance of the current with resistance which have been made. It seems more probable, however, that the value of  $R$  was in most cases so large in comparison with the resistance changes in the external circuit that the consequent changes in circuit have escaped notice. An examination of Goldmann's<sup>1</sup> data shows that he obtained a slightly smaller current when he used the larger resistance. From this the value of  $R$  for his cell can be estimated as of the order of 1.5 megohms.

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<sup>6</sup> Cottrell, *Z. physikal. Chem.*, **42**, 385 (1903).

## REVIEWS OF BOOKS.

**Textbooks of Physical Chemistry. Spectroscopy.** Vol. II. By E. C. C. BALY. (London: Longmans, Green & Co., Ltd. Pp. viii + 398, with 3 plates. 18s. net.)

This work on spectroscopy which was published originally in one volume is now being re-issued as four volumes—an indication of the enormous advance made in this department of Natural Science in recent years. In Vol. II., the author deals with the application of interference methods to spectroscopy, methods of exciting spectra, the various types of spectra and their characteristics, fluorescence and phosphorescence and spectro-photographic technique. The author has adopted an historical method of presentation, each chapter adequately presenting the developments leading to present ideas. The chapters on interference applications and on methods of illumination are good summaries, especially in the latter case, of details of processes scattered throughout scores of papers. King's important work with the electric furnace has been given an adequate treatment. The beginner will find a good deal of useful information about such matters as the filling of discharge tubes. No mention is made, however, of the usefulness of well-made copper-glass seals, nor is the efficiency of a palladium regulator, for *removal* of hydrogen from a tube subsequent to its sealing off, recorded. With regard to the control of a stream of gas the needle valve is probably much more convenient than the old capillary tube method.

The chapter on photography of the spectrum should be most valuable to the research worker and to all whose work involves the use of the photographic plate. The sensitising action of various dyes is clearly illustrated and the practical details given should be sufficient to enable the experimenter to prepare suitably sensitive plates, with a reasonable hope of success.

The chapter on the Nature of Spectra falls considerably below the standard of the others. After a good summary of some work on the fine structure of spectrum lines we are introduced in a very inadequate way to some spectra of hydrogen, carbon, oxygen, and nitrogen. Some of their band spectra are treated in unnecessary detail and others of considerable importance are not even mentioned. In no case is the modern quantum notation used, nor is mention made of the very important work done on several of these band spectra in the last two years. As a consequence several of the statements made in this connection are quite out of date.

Apart from this chapter, the book may be recommended to the advanced student who wishes to gain specialised knowledge of a rapidly growing branch of Science, as well as to the beginner in spectroscopic research who desires acquaintance with the wide and fascinating ramifications of his subject.

R. C. J.

**The Working of Aluminium.** By EDGAR T. PAINTON, B.Sc. (Eng.). (London, 1927: Chapman and Hall, Ltd. 13s. 6d. net.)

It does not take the reader of Mr. Painton's very useful book long to understand how aluminium, which the old generation remembers almost as a rare metal, could become an important material for the engineer and mechanician, as

soon as the electric furnace had made the old reduction processes of Wöhler, 1827, Ste. Claire Deville, Bunsen and Rose commercially possible, and as the alloys of aluminium, both with heavy metals (copper in the first instance) and the light metals (magnesium), had proved strong and relatively non-corrosive, as well as light. At present three times as much aluminium is wanted as before the war, and the development of automobiles and aircraft, chemical industry, and instrument-making will further increase the demand for the metal. One of the peculiarities of aluminium, which facilitates the pressing of heavy sheet into shells, is that the die can be applied continuously without the frequent intermediate annealing that shell and brass pressing requires. Mr. Painton ascribes this to the great durability of the metal; we should rather speak of plasticity.

The volume is chiefly concerned with the melting and mixing, casting, welding, soldering, drilling, repairing, etc., of aluminium and its alloys, in the form of sheet, wire, castings, and finished parts, and with their mechanical properties. Mr. Painton rightly does not burden his volume with references to the metallurgy of the metal and its history, and there is only a brief allusion to the work of Taylor and Elam on large crystals, in which the term "single crystals" does not occur. Single crystals are beginning to find application; they do not yet interest the metal worker, however, who will appreciate Mr. Painton's instructive data, notes on standard specifications and practical hints. Yet, as Mr. Painton very properly describes the protection of aluminium by anodic oxidation and electrolytic coatings of cadmium, he might have given a little more than the scanty remarks on corrosion in the introduction and in the notes on cooking utensils. But the metal worker will probably be glad on the whole that Mr. Painton has refrained from making excursions into the wide fields of the chemistry and the applications of aluminium, and has provided him with an eminently practical book of his own. The good diagrams and photographs illustrate mainly properties and working processes, not applications. Without detriment to the appearance of the book, however, the volume might have been made less bulky and heavy.

H. B.

**Aluminium: The Metal and its Alloys** (a critical descriptive treatise).

By M. G. CORSON. (London: Chapman & Hall, Ltd. Pp. xx + 291, with 122 plates. 1926. 36s. net.)

This book is a valuable contribution to the literature of aluminium and its alloys. It is, as its sub-title indicates, "a critical descriptive study" of the subject, but at the same time it needs to be read with discrimination, and is hardly suitable for the general reader "interested in aluminium," whether in industry or university.

Part I. deals with the properties of metallic aluminium largely in the form of tables and graphs. On the whole, the figures quoted leave little to be desired, but in certain cases, as, for example, the electrical resistivity, more recent values have now been generally adopted.

Part II. contains a description of the constitutional diagrams of forty-four binary and four ternary systems containing aluminium, and gives a list of certain other ternary systems of which the constitution is not fully known, indicating in each case specifically the problems awaiting solution. In the majority of cases the diagrams are up to date, but the work of the National Physical Laboratory on the constitution of the alloys of aluminium and iron, and that of the Research Staff of the Aluminium Company of America on the constitution of the aluminium

silicon alloys, seems to have been completely overlooked. The author has, however, taken liberties with some of the published diagrams, without stating the evidence on which his modifications are based, and he has included a number of imaginary diagrams, indicating the constitution of certain binary systems which have not yet been elucidated: these features are, in our opinion, greatly to be deprecated, and should certainly be omitted from future editions. They serve little useful purpose, and render it difficult for the uninitiated to realise how much is real and how much imaginary.

Part III., on the Technology of Aluminium Alloys, deals with the composition and properties of the more commonly used casting and forging alloys. The properties are given largely as tables and graphs, and are discussed in the light of the constitutional data given in the earlier part of the volume. The reasons for the various additions are carefully and critically explained, a most commendable feature, and one which renders this portion of the book both interesting and valuable. Certain alloys, such as those of the aluminium-copper-zinc-system and those of the aluminium-silicon system, with contents other than 13 per cent. of silicon, do not, however, receive the attention which they undoubtedly merit.

In Part IV., on Corrosion, the author gives a useful table of results showing the corrodibility of aluminium in various media. The author's work on the mechanism of the formation of a protective film on aluminium, and of its removal by various media, is worthy of the attention of all workers in this field. The section concludes with a series of comparative tests upon aluminium and various alloys. The theory of corrosion and its application to alloys is fully discussed, but so little is yet known about the constituents present in the more complex alloys, and of their electrochemical behaviour in the various combinations in which they may occur, that theories as to their comparative importance in determining the corrodibility of alloys must be treated with reserve.

Part V., Aluminium alloys in Engineering work, gives an account of the various applications of aluminium and its alloys in engineering practice. The requirements for any particular purpose are carefully explained, and the author indicates how far these requirements are met by various classes of alloys. The advantages and disadvantages of each class are critically discussed, and the selection of an alloy to suit a particular purpose is thus facilitated.

Part VI., dealing with the macro- and microstructure of aluminium and its alloys, is possibly the most interesting portion of the book, and is illustrated by a large number of excellent micrographs. After a brief description of the technique of polishing and etching, the author describes in detail the constituents present in aluminium and its alloys, and their behaviour with different etching reagents. As regards systems of which the constitution has been established on thermal grounds, the author's treatment is excellent, and forms a valuable contribution to the literature of the subject. His treatment of the theoretical portions of the subject, however, and his identification, by their appearance, of constituents in complex systems which have not yet been investigated, are very seriously open to criticism.

From what has been written above, it will be realised that this is, in many ways, a stimulating book for the specialist; its usefulness generally would be much enhanced by the omission of the features to which we have taken exception.

H. W. L. P. AND A. G. C. G.

## BOOKS RECEIVED.

**Elementary Electrical Engineering.** By ALBERT E. CLAYTON and HERBERT J. SHELLEY. (London, 1927 : Longmans, Green & Co., Ltd. Pp. ix + 410. 7s. 6d. net.)

**Reports of the Safety in Mines Research Board.** (London, H.M.S.O., 1927.)

(1) Fifth Annual Report of the Board including a report of matters dealt with by the Health Advisory Committee. (Price 9d.)

(2) Laboratory Methods of Determining the Inflammability of Coal Dusts by A. L. Godbert. (Price 1s. 6d.)

(3) The Study of Flame Movement by O. C. de C. Ellis. (Price 6d.)

(4) The Inflammation of Coal Dusts: The Effect of the Chemical Composition of the Dust by T. N. Mason and R. Y. Wheeler. (Price 6d.)

(5) A description of the Safety in Mines Research Station, Buxton. (Price 6d.)

(6) The Ignition of Gases by Hot Wires by W. C. F. Shepherd and R. Y. Wheeler. (Price 1s.)

**The Scientific Work of the late Spencer Pickering, F.R.S.** By PROFESSOR T. M. LOWRY, F.R.S. and SIR JOHN RUSSELL, F.R.S., with a biographical notice by PROFESSOR A. HARDEN, F.R.S. (London, 1927. For the Royal Society Harrison & Sons, Ltd. Pp. ix + 247. 4s. net.)

The first part of the volume is devoted to a review of Pickering's work along the more academic lines of chemistry and physics, and concludes with an annotated bibliography of his 130 contributions of this nature to scientific literature.

The final pages deal with his contributions to agriculture and in particular the work at the Woburn experimental fruit farm.

**The Elements of Telephone Transmission.** By H. H. HARRISON, M.I.E.E. (London : Longmans, Green & Co., Ltd. Pp. vii + 147. 5s. net.)

# THE DECOMPOSITION OF TRIETHYL SULPHONIUM BROMIDE IN MIXED SOLVENTS.

By ROBERT FREDERICK CORRAN.

(Communicated by PROFESSOR W. C. M. LEWIS.)

(Received 24th August, 1927.)

The kinetics of the decomposition of triethyl sulphonium bromide in a number of single solvents have been investigated very thoroughly by von Halban.<sup>1</sup> Subsequent work by Taylor and Lewis<sup>2</sup> has shown that there is satisfactory agreement between the infra-red absorption bands, observed spectroscopically, and those calculated from the critical increments derived from von Halban's data. All the available evidence goes to show that the decomposition of triethyl sulphonium bromide follows a simple uni-molecular equation. It is therefore a convenient reaction to employ in connection with the influence of environment upon the rate of chemical change.

An account is here given of the results obtained with certain mixed solvents which serve at the same time to bring out a point of some importance in connection with the relation which exists between reaction rate and critical increment of activation.

## Experimental.

Two series of experiments have been carried out. In the one, the solvent was benzyl alcohol plus glycerol, in the other, benzyl alcohol plus toluene. Glycerol and toluene were used because of their widely different physical properties (*e.g.*, viscosity and dielectric constant) and also because both liquids are miscible in all proportions with benzyl alcohol.

The triethyl sulphonium bromide was prepared at the outset by the method of Taylor and Lewis,<sup>2</sup> but this mode of preparation proved to be long and tedious. The salt was therefore prepared by maintaining a mixture of ethyl sulphide and ethyl bromide at a temperature of 38.4° C. (this temperature being slightly below the boiling-point of ethyl bromide) for seven days. The crystals of triethyl sulphonium bromide, which had formed, were then purified from ethyl bromide and ethyl sulphide by precipitating the salt from alcoholic solution by means of ether. The crystals were kept in a vacuum desiccator pending use.

The method used in following the reaction was similar to that of von Halban, *i.e.*, by introducing a definite volume of the salt in the solvent under investigation into a number of test-tubes, the latter being then sealed off. The amounts of solution used varied from 2 c.c. for the more concentrated solutions, to 5 c.c. for the less concentrated solutions. It is interesting to note that, whereas the addition of glycerol increased the

<sup>1</sup> *Z. physikal. Chem.*, **67**, 129, 1909.

<sup>2</sup> *Trans. Chem. Soc.*, **121**, 665, 1922.

solubility of the sulphonium bromide, the addition of toluene decreased the solubility of the salt. All the test-tubes were then immersed in a thermostat at the most suitable temperature (previously determined), in this case 80° C. and 90° C. respectively and, at the beginning of the reaction and subsequently at regular intervals during the course of the reaction, a test tube was withdrawn, cooled in ice and the unchanged triethyl sulphonium bromide estimated by shaking the contents with a mixture of ether and water in a separating funnel. The aqueous layer, containing the unchanged triethyl sulphonium bromide, was then separated and the ethereal layer washed twice with water to ensure complete extraction of the sulphonium bromide. The latter was finally estimated by addition of excess standard silver nitrate and back-titration of the latter with standard ammonium thiocyanate.

The benzyl alcohol used was first dried over anhydrous sodium sulphate and redistilled, the portion used distilling at 206° C. The glycerol was distilled at 15 mm. pressure at 190° C., the glycerol distilling thus without any decomposition. Toluene was dried over sodium wire for twenty-four hours and redistilled, the portion used distilling at 110° C. at 760 mm. The solutions under investigation, containing high concentrations of glycerol, were measured out by weight instead of by volume.

The composition of the benzyl alcohol + glycerol mixtures used in the first series of experiments is given in Table I. The benzyl alcohol-toluene mixtures used in the second series are given in Table IV.

In general, the reaction in organic solvents reaches an end point which corresponds with the complete decomposition of the salt. With pure glycerol as solvent, however, no sensible decomposition can be observed.

It was found that the addition of glycerol to benzyl alcohol caused a displacement of the point of equilibrium between reactant (triethyl salt) and resultants indicated by the equation :—



towards the side of the reactant, *i.e.*, in the direction characteristic of the equilibrium in pure glycerol solution itself. Consequently it was found necessary to determine equilibrium constants for the reaction in the different benzyl alcohol + glycerol mixtures at both temperatures. These were found by maintaining a known volume of the solution of triethyl sulphonium bromide in the given solvent at the temperature required until equilibrium was attained. The time of immersion was in all cases ten times the period of half decomposition of the sulphonium bromide. The initial and equilibrium concentrations of the sulphonium bromide were determined in the manner previously outlined, the values of the equilibrium constants being given by the expression :—

$$K = \frac{(\text{C}_2\text{H}_5)_3\text{SBr}}{(\text{C}_2\text{H}_5)_2\text{S} \times \text{C}_2\text{H}_5\text{Br}}$$

The concentrations are expressed in moles per litre in every case. Table I. gives the values of K for each solvent at the two temperatures.

The expression for the unimolecular velocity constant was then corrected for a bimolecular reverse reaction as follows. If we denote the initial concentration of triethyl sulphonium bromide by *a* mols. per litre and the amount decomposed after a time *t* by *x*, we obtain :

$$-\frac{dx}{dt} = k_1(a - x) - k_2x^2$$

TABLE I.

Composition of Solvent.				K <sub>90</sub> °.	K <sub>90</sub> °.	Q (Heat Absorbed in Dissociation of the Salt.)
Mass Per Cent.		Molar Per Cent.				
Benzyl Alcohol.	Glycerol.	Benzyl Alcohol.	Glycerol.			
100.00	0.00	100.00	0.00	1.64	1.22	7,500
90.23	9.77	88.74	11.26	4.91	3.70	7,200
80.39	19.61	77.74	22.26	14.32	11.10	6,500
69.39	30.61	65.46	34.54	42.49	34.01	5,700

where  $k_1$  and  $k_2$  are the rates of the forward and reverse reactions respectively. Since  $K = k_2/k_1$ , we obtain :

$$k_1 = \frac{1}{tC} \log \frac{(1-C)(2Kx+1+C)}{(1+C)(2Kx+1-C)} \quad \text{where } C = \sqrt{1+4aK}.$$

As an instance of the applicability of this equation, the uncorrected and corrected velocity constants at 90° C. using benzyl alcohol containing 34.54 molar per cent. glycerol are given in Table II.

TABLE II.

$t$ (Mins.).	$(a-x)$ C.c. $\text{NH}_4\text{CNS}$ .	$(a-x)$ Mols./Litre.	$k_{\text{obs}} \times 10^5$ .	$k_{\text{corr}} \times 10^5$ .
0	18.61	0.08496	—	—
230	16.56	0.07560	0.844	0.854
408	15.02	0.06857	0.875	0.919
572	14.02	0.06400	0.828	0.905
702	13.48	0.06155	0.766	0.864
819	12.83	0.05857	0.756	0.899
1112	12.11	0.05530	0.644	0.831
Mean			0.785	0.879

The final values of the corrected velocity constants in benzyl alcohol + glycerol mixtures are given in Table III., time being expressed in seconds and logarithms to the base  $e$ . In the case of benzyl alcohol + toluene mixtures, Table IV., no correction is necessary as the reaction goes to completion.

TABLE III.

Solvent. Molar Per Cent.		$k_{90}^{\circ} \times 10^5$ .	$k_{90}^{\circ} \times 10^5$ .	E in Cals. Per Mole.
Benzyl Alcohol.	Glycerol.			
100.00	0.00	1.480	6.075	35,900
88.74	11.26	0.720	2.83	34,800
77.74	22.26	0.444	1.695	34,100
65.46	34.54	0.233	0.882	33,900

The reaction velocities were determined in duplicate in every case, but only the mean values are quoted.

## 608 DECOMPOSITION OF TRIETHYL SULPHONIUM BROMIDE

*Discussion of Results.*—Considering the effects of glycerol and toluene respectively on the velocity of decomposition, it will be observed that, whereas the addition of glycerol causes a progressive lowering of the velocity constant, the addition of toluene causes a progressive increase.

TABLE IV.

Solvent. Molar Per Cent.		$k_{90}^{\circ} \times 10^5.$	$k_{90} \times 10^5.$	E in Cals. Per Mole.
Benzyl Alcohol.	Toluene.			
100'00	0'00	1'480	6'075	35,900
75'25	24'75	3'178	12'51	34,800
50'34	49'66	7'796	28'59	33,100
25'26	74'74	24'45	88'32	32,700

From the observed velocity constants, the critical increments for the decomposition in the various solvents can be calculated by means of the equation,

$$\frac{d \log k}{dt} = \frac{E}{RT^2}.$$

Values of E thus calculated have been included in Tables III and IV.

Assuming that a unimolecular reaction consists of the spontaneous decomposition of the activated reactant, the general expression for the unimolecular velocity constant takes the form  $k = Se^{-E/RT}$ . If S is independent or approximately independent of the physical properties of the mixed solvents, we would expect that an increase in the velocity constant would be accompanied by a decrease in the critical increment. This is so in the case of benzyl alcohol + toluene mixtures, the addition of toluene causing an increase in  $k$  and a diminution in E. In the case of benzyl alcohol + glycerol mixtures, on the other hand, as the velocity constant falls, the calculated critical increment also falls. The addition of glycerol to the solvent would appear therefore to introduce an "anomaly" in either the observed velocity constants or the apparent critical increments. The fact that in both series of solvents an appreciable variation in the apparent critical increments is observed would suggest that the stability of the triethyl sulphonium bromide molecule is altered by the addition of toluene and glycerol respectively. Such a variation in stability should manifest itself in the infra-red absorption bands of the sulphonium bromide in the solvents employed. This conclusion does not imply that the chemical change is due to absorption of radiation. The measurement of the infra-red absorption bands and the treatment of the "anomaly" from the point of view of infra-red absorption spectra is taken up in the next section.

### The Infra-Red Absorption Spectra of Triethyl Sulphonium Bromide in the Different Solvent Mixtures.

From the magnitude of the observed critical increments, it was expected that a characteristic absorption band would lie in the very short wave-length region of the infra-red, a region in which it is difficult to measure absorption bands with accuracy.

The method and precautions employed in the determination of the absorption bands were those of Taylor and Lewis<sup>2</sup> with the modification

that the radiomicrometer was replaced by a thermopile and Moll Galvanometer. The latter instrument proved to be very efficient although it was extremely susceptible to atmospheric conditions. The greatest difficulty experienced in the present work was that the intensity of light of wave-lengths between  $0.7\mu$  and  $1.00\mu$  was small, and consequently a high degree of accuracy was necessary in the readings of the deflexions of the galvanometer. The absolute magnitude of the deflection was of the order 3 to 7 cms. and the change therein for  $0.2\mu$  change in wave-length corresponded with  $0.3 - 0.5$  cm. approximately.

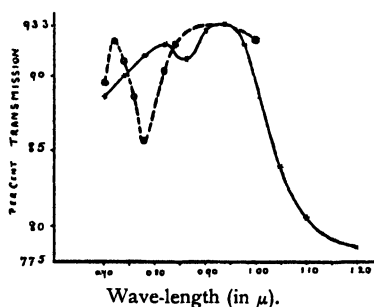


FIG. 1.—Composition of solvent, 100 per cent. benzyl alcohol.

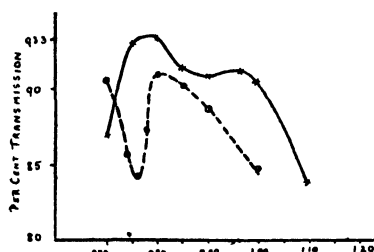


FIG. 2.—Composition of solvent, 88.74 per cent. benzyl alcohol + 11.26 per cent. glycerol.

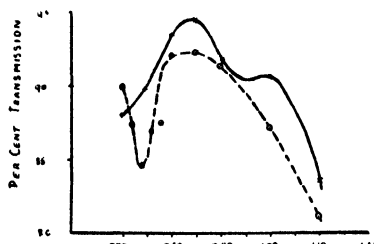


FIG. 3.—Composition of solvent, 77.74 per cent. benzyl alcohol + 22.26 per cent. glycerol.

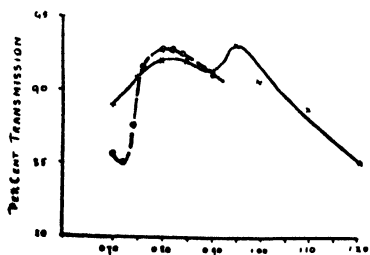


FIG. 4.—Composition of solvent, 65.46 per cent. benzyl alcohol + 34.54 per cent. glycerol.

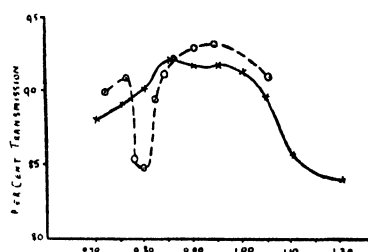


FIG. 5.—Composition of solvent, 75.25 per cent. benzyl alcohol + 24.75 per cent. toluene.

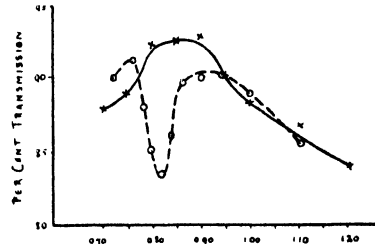


FIG. 6.—Composition of solvent, 50.34 per cent. benzyl alcohol + 49.66 per cent. toluene.

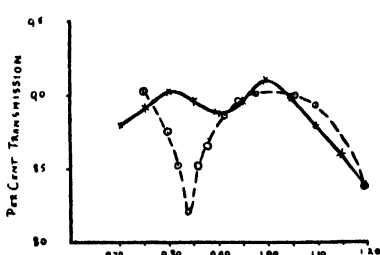


FIG. 7.—Composition of solvent, 25.26 per cent. benzyl alcohol + 74.74 per cent. toluene.

## 610 DECOMPOSITION OF TRIETHYL SULPHONIUM BROMIDE

The solubility of the triethyl sulphonium bromide in the solvents is of the order of tenth normal with respect to the solute and consequently the variations in the percentage transmission at the head of the band, and away from the band, are not great. They are, however, sufficiently distinct to identify without doubt the position of the band. The accompanying curves, Figs. 1-7, give the absorption bands for the different solvents (full lines) and solutions (broken lines) over the range  $0.70\mu - 1.20\mu$ .

Tables V. and VI. give the values of the observed wave-lengths of the band head and also the wave-lengths calculated from the equation  $E = N/h\nu$ , where  $E$  is the observed critical increment obtained from the temperature coefficient of the reaction velocity constants, and in the last column the critical increment regarded as the true increment calculated from the actual position of the band head.

TABLE V.

Solvent. Molar Per Cent.		E <sub>calcd.</sub> from Temp. Coeff.	Wave-Length (Calcd.) (from Previous Column).	Wave-Length (Obs.).	E <sub>true</sub> .
Benzyl Alcohol.	Glycerol.				
100.00	0.00	35,900	0.79 $\mu$	0.78 $\mu$	36,300
88.74	11.26	34,800	0.81 $\mu$	0.76 $\mu$	37,100
77.74	22.26	34,100	0.83 $\mu$	0.74 $\mu$	38,200
65.46	34.54	33,900	0.84 $\mu$	0.72 $\mu$	39,500

TABLE VI.

Solvent. Molar Per Cent.		E <sub>calcd.</sub> from Temp. Coeff.	Wave-Length (Calcd.) (from Previous Column).	Wave-Length (Obs.).	E <sub>true</sub> .
Benzyl Alcohol.	Toluene.				
100.00	0.00	35,900	0.79 $\mu$	0.78 $\mu$	36,300
75.25	24.75	34,800	0.81 $\mu$	0.80 $\mu$	35,400
50.34	49.66	33,100	0.85 $\mu$	0.82 $\mu$	34,600
25.26	74.74	32,700	0.87 $\mu$	0.84 $\mu$	33,700

Considering first the results for the benzyl alcohol + toluene mixtures, it will be seen that the agreement between the observed wave-length and that calculated from the critical increment as given by the temperature coefficient is fairly good, bearing in mind the experimental difficulties, and we may therefore conclude that in benzyl alcohol + toluene mixtures, the stability of the triethyl sulphonium bromide molecule is equally well expressed by the absorption band and by the critical increment of decomposition, as obtained from the temperature coefficient.

For the case of the benzyl alcohol + toluene mixtures it is of interest to calculate the value of  $S$  which occurs in the general type equation  $k = Se^{-E/RT}$ , the values of  $E$  being those given in the final column of Table VI. and  $k$  the observed velocity constant at  $80^\circ \text{C}$ . (Table IV.), to see whether  $S$  alters appreciably or not. In the case of a unimolecular process  $S$  has the dimension of time $^{-1}$ . The following results are obtained.

Molar per cent. of toluene:	0.0	24.75	49.66	74.74
$S \times 10^{-17}$	4.57	2.77	2.15	1.81

It will be observed that  $S$  remains of the same order of magnitude throughout. Whether the fall in the values is significant or not it is difficult to say, for the total change in  $S$  lies within the experimental error of the values ascribed to  $E_{\text{true}}$ . (Thus in order to alter  $S$  from  $1.81 \times 10^{17}$  to  $4.57 \times 10^{17}$  it is only necessary to assume that  $E = 34,300$  calories in place of the value actually employed, *viz.* 33,700, or otherwise expressed, the position of the band head required is  $0.83\mu$  instead of the observed value  $0.84\mu$ .)

The first inference to be drawn from the approximate constancy of the  $S$  values is that volume concentration terms of the triethyl salt (which have been employed in the determination of the  $k$  values) are legitimate quantities to use, or in other words that the activity values in this case—if activity be involved—may be replaced by such terms. (Incidentally activity values based on solubility would have led to values of  $k$  which would in turn have required greater variation in  $S$ .)

The second inference to be drawn is that the magnitude of  $S$ , of the order  $10^{17}$ , is so very great that it cannot be attributed to any frequency term characteristic of any type of motion within the molecule which would be likely to be involved in chemical change in the ordinary sense. It follows therefore that  $S$  is not a single term but rather the product of two or more. Incidentally this value of  $S$  is many times greater than that found for the unimolecular decomposition of nitrogen pentoxide in certain organic solvents, namely of the order  $10^{14}$ , which is likewise characteristic of unimolecular reaction in the gaseous state.

In the benzyl alcohol + glycerol mixtures, it will be seen that the addition of glycerol causes a progressive shift in the infra-red absorption band towards shorter wave-lengths. Moreover as the glycerol concentration increases, the divergence between the observed and the calculated infra-red wave-lengths (obtained from the temperature coefficient of the reaction velocity) becomes more pronounced. The absorption spectra indicate that the effect of glycerol differs from that of toluene in that it renders the molecule of the triethyl salt more stable, whereas the addition of toluene renders it less stable. The relative positions of the band head taken as a measure of stability would lead us to expect that in the case of the benzyl alcohol + glycerol mixtures the velocity of decomposition of the triethyl salt should decrease with increase in glycerol content, a conclusion in agreement with experiment. In this case, therefore, the anomaly between critical increment and velocity constant reduces to a failure of the observed velocity constants to give a true value for the critical increment.

The writer has not succeeded in obtaining a satisfactory explanation of the effect referred to. A number of possibilities have been considered, for example the introduction of a viscosity term (which necessitated the determination of the viscosities of the various mixtures at the reaction temperatures), the introduction of considerations based on dielectric constant (since it is reasonable to believe that the relative amounts of the polar (ionisable) and non-polar form of the triethyl salt would depend upon the dielectric capacity and it is the non-polar form which alone decomposes into alkyl halide and sulphide) and the possible formation of glycerol-triethyl salt complexes. None of these possibilities, however, in so far as the writer has been able to deal with them, seem capable of altering the relative positions (with increasing glycerol content) of the velocity constant curves at two different temperatures in the direction required to account for and eliminate the anomaly, namely the conversion of the slight convergence actually exhibited by the curves into a small divergence such as is required by the general downward trend of the velocity constant curve

(at a given temperature) as well as by the observed positions of the band head in the various solvent mixtures.

The only fact which seems to bear even indirectly upon the difference in behaviour of glycerol and toluene respectively in relation to triethyl sulphonium bromide is that the addition of glycerol (to benzyl alcohol) increases the solubility of the salt whilst the addition of toluene decreases the solubility.

Leaving aside the problem of attempting to account for the anomaly referred to, it appears reasonable to conclude that the positions of the band heads in the short infra-red region afford in the present case the most reliable values for the true critical increments. These values calculated from the band heads are recorded in the final columns of Tables V. and VI.

The calculation of the  $S$  term in the case of benzyl alcohol + glycerol mixtures shows that this term increases fairly rapidly with increase in glycerol content. Thus in the absence of glycerol  $S = 4.57 \times 10^{17}$  whilst with 34.54 molar per cent.  $S = 6.88 \times 10^{18}$ . This variation is real in that it lies outside the experimental error involved in the band head measurement of  $E_{\text{true}}$ . (Thus in order to convert the latter value of  $S$  into the former, it would be necessary to take  $E = 37,600$  calories ( $\lambda = 0.755\mu$ ) instead of  $E = 39,500$  ( $\lambda = 0.72\mu$  observed).)

### The Effect of the Removal of Dust on the Velocity of Decomposition of Triethyl Sulphonium Bromide in Propyl Alcohol.

In a recent paper, F. O. Rice<sup>3</sup> has shown that, in a number of reactions, studied by him, dust particles ordinarily present in all solutions exert a marked catalytic activity. For example the decomposition of hydrogen peroxide in aqueous solution and the oxidation of sodium sulphite are almost completely suspended when special care is taken to remove the dust from the solution.

In view of this it was considered of interest to determine the rate of decomposition of triethyl sulphonium bromide in a suitable organic solvent, namely propyl alcohol, both solvent and solution being freed as far as possible from dust and the reaction carried out in an atmosphere of dust free air.

#### *Experimental.*

**Dust Free Solvent.**—The dust free solvent was prepared by the distillation method of Martin<sup>4</sup> which has been employed by Rice and found to be satisfactory. The distillation and rinsing process was repeated, on the average, nine times, in order to ensure that the liquid finally in the bulb was dust free. The amount of dust was observed qualitatively by concentrating an intense beam of light from an arc lamp on the vessel and observing the Tyndall effect. Examination of the solution after each distillation showed that the amount of dust decreased until, after about nine distillations, the liquid was entirely dust free, as far as the method of observation could ascertain.

**Dust Free Air.**—The method of preparation of 'dust free' air was essentially that of Dewar,<sup>5</sup> and was based on the fact that when a current of air is passed through a vessel containing cotton wool previously saturated with glycerol, the latter removes dust from the air.

<sup>3</sup> *J. Amer. Chem. Soc.*, **48**, 2099, 1926.

<sup>4</sup> *J. physical Chem.*, **24**, 478, 1920.

<sup>5</sup> *Proc. Roy. Inst.*, **22**, 179, 1918.

A current of air was passed through three towers, the first containing a mixture of lime and anhydrous sodium carbonate, the second containing soda lime and the third closely packed cotton wool, previously thoroughly saturated with glycerol. The first tower removed water vapour, the second carbon dioxide and the third dust from the air passing through them. Examination by the Tyndall cone method, of the air itself and of a purified solvent through which the air was drawn showed that this method was satisfactory since no evidence of dust was found in the air treated in the above manner.

*Dust Free Solutions.*—In the first place it was necessary to have the solid solute freed from dust. This was done by suspending the solute in dry ether in a vessel which was eventually joined to the principal apparatus and passing a current of dry, dust free air through the mixture. The agitation caused by the passage of the gas removed the dust from the solute and this was carried away in the ether vapour with the current of air. This procedure was repeated four times and the resulting solid sulphonium bromide taken as 'dust free'. The solid salt was shaken into the reaction vessel, the operation being carried out in an atmosphere of dust free air. The resulting solution was shown to be 'dust free' by the Tyndall cone test. The reaction vessel was fitted with a tap, through which portions of the liquid could be extracted for analysis at intervals during the run. Lubricating grease could not be used, the tap being surrounded by a vessel of mercury. Whilst still connected to the supply of dust free air, the whole apparatus was immersed in a thermostat at the temperature of investigation, in this case 80° C., and the reaction followed in the manner previously described. The solution was extracted *via* the tap and the volume of solution was replaced by a quantity of dust free air, so that no dust was introduced into the reaction vessel during the various readings. The results below give the velocity constants using solutions largely freed from dust and also using solutions of triethyl sulphonium bromide in propyl alcohol from which no attempt was made to remove dust.

TABLE VII.

Solvent.	Expt. No.	$k_{80^\circ} \times 10^6$ .
Propyl alcohol containing dust . .	I	2.748
" " " " " " . .	II	2.756
Propyl alcohol freed from dust . .	III	2.739
" " " " " " . .	IV	2.743
" " " " " " . .	V	2.750

The values recorded in the above table are the same, within the limits of experimental error. This case is therefore apparently analogous to the 'unimolecular' *gaseous* reaction examined by Rice and shown to be independent of the presence of dust. Whether this feature is general or not is unknown. It may be pointed out that the results of the dust removal experiments afford no clue to the anomaly dealt with earlier in this paper.

### Summary.

1. The unimolecular velocity constants of the decomposition of triethyl sulphonium bromide into diethyl sulphide and ethyl bromide have been determined at 80° C. and 90° C. in mixed solvents containing benzyl alcohol + toluene and benzyl alcohol + glycerol respectively. The presence

of glycerol causes the reaction to reach an equilibrium point. The corresponding equilibrium constants at 80° C. and 90° C. have been determined and with their aid a corrected velocity constant of decomposition obtained. It is found that whilst the toluene increases the rate of decomposition the glycerol decreases it.

2. From the temperature coefficients of the reaction it is found that the (apparent) critical increments of activation fall in value as the content of either toluene or glycerol in the benzyl alcohol is increased. The direction of change in the case of benzyl alcohol + toluene mixtures is therefore that which would be anticipated on theoretical grounds in view of the observed change in the velocity constant with solvent composition. On the other hand the behaviour in benzyl alcohol + glycerol mixtures is anomalous.

3. With the object of throwing some light on the anomaly the absorption spectra exhibited by the triethyl salt in the short infra-red region in the various solvent mixtures have been determined by means of a Hilger infra-red spectrometer, Moll galvanometer and thermopile. It is found that the position of the head of the band varies with the composition of the solvent. In the case of benzyl alcohol + toluene mixtures the shift in the position of the band head is in satisfactory agreement with the alteration in the observed critical increment. In the case of benzyl alcohol + glycerol mixtures the head of the band shifts towards the shorter wave-length whilst the change calculated from the critical increment is in the opposite direction. The direction of shift of the band is that which would be expected from the effect of glycerol upon the velocity constant (at a given temperature). It is concluded therefore that the band head gives the true critical increment.

4. The decomposition of triethyl sulphonium bromide in propyl alcohol has been investigated under conditions which permit of the extensive removal of the dust ordinarily present in all solutions. It is shown that no effect is produced upon the velocity of decomposition, the behaviour in this case being analogous to that found by F. O. Rice for the (unimolecular) decomposition of gaseous nitrogen pentoxide.

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## THE STRUCTURE AND FORMATION OF COLLOIDAL PARTICLES.

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Three main points have to be discussed in regard to the structure of colloidal particles. State of aggregation, crystalline form and shape.

*State of aggregation and crystalline form* may be investigated with the

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help of X-ray diagrams. The method of Debye and Scherrer and of Hull is generally used, the X-rays striking a jet of the colloidal solution or a rod made of the colloidal particles. If the particles are crystalline and not orientated, they show a diagram with distinct lines. If crystalline particles are orientated, for instance round an axis as in most fibres, they show a diagram with dark spots instead of the lines. If the particles are amorphous, their diagrams show a uniform darkening or broad bands. The particles of gold and silver sols are crystalline and have the same crystalline form as the heavy metals; the same holds for the particles of  $\text{CuO}$ ,  $\text{V}_2\text{O}_5$  and of  $\text{Fe}_2\text{O}_3$  sols prepared by oxidising  $\text{Fe}(\text{CO})_5$  with  $\text{H}_2\text{O}_2$ , if they are of sufficient age. The well-known sols prepared by dialysing  $\text{FeCl}_3$  solutions give mainly a diagram of a basic iron chloride; some sols of high age also contain rhombic particles of goethite  $\text{FeO}(\text{OH})$ . Freshly prepared sols of many oxides like  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{ThO}_2$  have particles that show an amorphous diagram. This is also the case for colloidal solutions of sulphur and  $\text{As}_2\text{S}_3$ .<sup>1</sup>

The two states of aggregation mentioned so far, the crystalline and the amorphous solid state, are not the only ones which we must distinguish. We must also take into consideration the state for which Friedel<sup>2</sup> has used the general term "mesomorphous"; the so-called crystalline liquids are the best known example of this mesomorphous condition. Molecules having a distinct elongated axis may lie for instance symmetrically around a central axis, their own axis being parallel to the central axis, the position of each molecule being otherwise quite accidental. Or they may be piled in layers, again with their own axes parallel to one another, the position of the molecules belonging to a single layer being haphazard. Phases of this kind do not give an X-ray diagram with distinct lines as do crystalline phases, for the molecules are not orientated in the strict order of a space-lattice. It is possible that we may find lines in one direction, but not in all. Optical methods are generally preferable to distinguish mesomorphous phases from other states of aggregation. We know quite a number of colloidal solutions whose particles are most likely in a mesomorphous state, such for example, as solutions of soaps, of lecithin, of salvarsan, and of mercurisulfosalicylic acid.<sup>3</sup>

The *shape* of the particles cannot be derived from X-ray measurements, but many optical methods are of value. Most of them only allow us to decide the question, whether the particles are practically spherical—*i.e.*, whether their dimensions in all three directions are about of equal length—or whether they are distinctly non-spherical. Particles of these two groups exhibit differences in the behaviour of their diffracted light in the ultra-microscope. Non-spherical particles, *e.g.*, particles of a rod-like shape, exhibit pronounced scintillations and not a continuous radiation of light as is the case with spherical particles. The cause of this scintillation has been determined by Siedentopf<sup>4</sup> for microscopical cases and the same consideration holds for the behaviour of the particles in the ultramicroscope.<sup>5</sup> An elongated particle can be seen in the ultramicroscope only when the light rays strike the particle perpendicularly to its longitudinal axis and when the particle

<sup>1</sup> Boehm, *Kolloid Z.*, **42**, 276 (1927).

<sup>2</sup> Friedel, *Ann. Physique*, **18**, 358 (1922); see also Alexander, "Colloid Chemistry," p. 102 (1926).

<sup>3</sup> Sophie Berkman and Zocher, *Kolloidchem. Beih., Ambros, Festschr.*, **23**, 292 (1926); *Kolloid Z.*, **42**, 309, 322 (1927); Freundlich, Stern, and Zocher, *Biochem. Z.*, **138**, 307 (1923).

<sup>4</sup> Siedentopf, *Z. wiss. Mikroskopie*, **24**, 104 (1907); **25**, 424 (1909); **29**, 1 (1912).

<sup>5</sup> Szegvari, *Physik. Z.*, **24**, 91 (1923); *Z. Physik*, **21**, 348 (1924); *Z. physikal. Chem.*, **112**, 277, 295 (1924).

lies in the plane of observation in the microscope. As a rule, if the light strike the particle in a direction parallel to its longitudinal axis or if the particle be perpendicular to the plane of observation, it cannot be seen. Since the particles have a Brownian movement they become luminous when in the correct position and disappear in all other positions. This gives rise to scintillations.

It is possible to intensify this effect by using the cardioid ultramicroscope with certain diaphragms. Siedentopf<sup>6</sup> already has used the azimuth diaphragm in researches with the microscope. Szegvari<sup>5</sup> was the first to introduce it for ultramicroscopic investigations. The applicability of the azimuth diaphragm depends upon the phenomenon just mentioned, that elongated particles are visible in the ultramicroscope when the light strikes them perpendicularly to their longitudinal axis and when they lie in the plane of observation. In the slit ultramicroscope, the light always enters in a definite direction which cannot be changed at will. In the cardioid ultramicroscope, on the other hand, this may be done. In this instrument the light rays enter the cell from all sides. If an azimuth diaphragm, that is a moveable slit diaphragm, is introduced under the condenser, then by turning

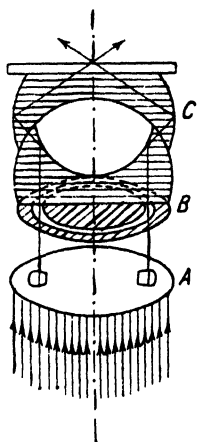


FIG. 1.

ing the diaphragm, the light can be made to strike the ultramicroscopic preparation from any desired direction. Fig. 1 shows the use of the azimuth diaphragm diagrammatically, A being the moveable slit diaphragm. Fig. 2\* represents its true form, with the handle the diaphragm is turned, with the screw the slit-holes may be made wider or narrower. Although the details will not be discussed here, Szegvari has shown that in the use of the azimuth diaphragm, a suitable aperture must be employed. He therefore always uses the azimuth diaphragm together with a suitable aperture diaphragm, an iris diaphragm, which enables him to obtain the correct setting of the aperture.

If these diaphragms are used for a sol with rod-like particles then the scintillations are distinctly more intense than those observed in the slit ultra-microscope. This is caused by the fact that the optical conditions are better suited for the observation of the scintillations.

If we use a gel we observe no scintillations because the particles do not move but they are only visible when the light strikes them in the proper direction.

Some macroscopic methods of investigation depend on the fact that the optical properties of sols with non-spherical particles change, if the sol is made to flow. The non-spherical shape of the particles is mostly due to the fact that the particles are crystalline (or mesomorphous). If they are elongated, they generally belong to a crystalline group which shows double refraction. As long as the sol is at rest with its particles lying quite irregularly, in consequence of their Brownian movement, the fluid will have no double refraction, the birefringence of particles lying in one direction being neutralised by particles of an opposite direction. But as soon as the sol is made to flow, the particles are orientated in a certain direction. The viscous and elastic properties of these sols are the main cause of this orientation. The flowing sol is distinctly birefringent. If it flows for instance through a tube with parallel walls, it exhibits fluxional birefringence

<sup>6</sup> Siedentopf, *Z. wiss. Mikroskopie*, **25**, 424, (1909).

\* Facing p. 622.

similar to the lamella of a uniaxial crystal which has been cut parallel to its axis and whose axis lies in the direction of flow.<sup>7</sup>

The investigation of this fluxional birefringence provides a valuable method for detecting the shape of colloidal particles. It is generally used in a convenient form proposed by Zocher<sup>8</sup> (Fig. 3). Light which is polarised by reflection passes through the colloidal solution and is analysed by a Nicol prism. The sol is in a cylinder and is made to rotate. The particles of a sol which show fluxional birefringence are orientated more or less in concentric circles and therefore a dark cross appears, if the planes of polarisation are crossed. This is shown diagrammatically in Fig. 4. In Fig. 5\* are photographs of such dark crosses. This method is very sensitive. In the case of  $V_2O_5$  sol—a deep red-brown fluid whose particles

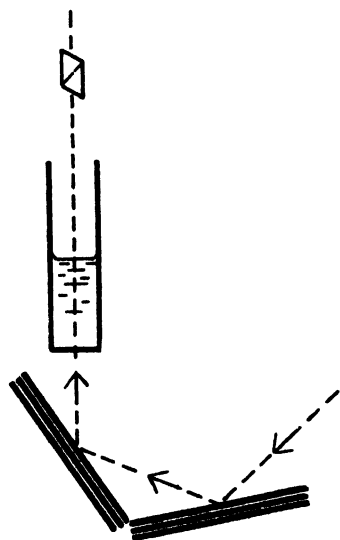


FIG. 3.

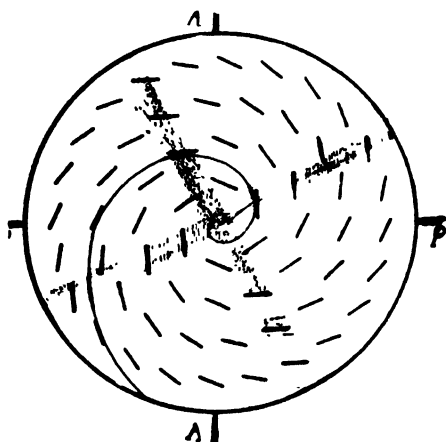


FIG. 4.

are distinctly needle-shaped—the fluxional birefringence is still visible when the fluid is practically colourless.

The Tyndall effect of sols with non-spherical particles is also influenced by flowing, because, as mentioned before, the amount of light diffracted by the particles depends upon the position of the axis of the particles towards the direction of the incident light. When the direction of the incident polarised light, the direction of its electrical vector and the direction of flow are changed, the intensity of the Tyndall effect is also changed, in such a way that it is possible to distinguish between particles which are needle-shaped, that is elongated only in one direction, and those which are plate-like, that is elongated in two directions.<sup>9</sup>

Another method which generally only allows us to decide whether the particles are spherical or not is the state of polarisation of the Tyndall-light of sols at rest.<sup>10</sup>

<sup>7</sup> Dieselhorst, Freundlich and Leonhardt, *Elster-Geitel Festschr.*, 1915, p. 453.

Dieselhorst and Freundlich, *Physik. Z.*, 16, 422 (1915).

Freundlich, *Z. Electrochem.*, 22, 27 (1916).

<sup>8</sup> Zoher, *Z. physikal. Chem.*, 98, 293 (1921).

<sup>9</sup> Dieselhorst and Freundlich, *Physik. Z.*, 17, 117 (1916).

<sup>10</sup> Ettisch, Farmer, Loeb and Lange, *Biochem. Z.*, 184, 257 (1927).

\* Facing p. 622.

By comparing the refraction or absorption of a colloidal solution with the values of these quantities calculated from the refraction or absorption of the particles and of the medium of dispersion, it is likewise possible to draw conclusions about the shape of the particles. For instance, according to a theory of Wiener,<sup>11</sup> the refraction of a system consisting of very small particles with index of refraction  $n_1$  in a medium with index of refraction  $n_2$  is given by the formula

$$\frac{n_m^2 - n_2^2}{n_m^2 + u} = \phi \frac{n_1^2 - n_2^2}{n_1^2 + u}.$$

In this formula  $n_m$  is the index of refraction of the mixture that is the colloidal solution,  $\phi$  is the relative volume of the particles,  $u$  a factor which depends on the shape of the particles. If they are spherical,  $u$  has a value equal to  $2n_2^2$  that is 3.55. Measurements by Frey<sup>12</sup> with gelatine solutions gave a value for  $u$  in one case of 3.90, in a second of 3.51. This is a good verification of the assumption that the particles are spherical. A gelatine gel on the other hand may be made birefringent by stress or pressure, and the same holds good for a gelatine solution if it is rotated very rapidly. We must assume that, under these conditions, particles which were originally spherical are deformed.

The results of measurements of this kind so far are the following:

Spherical particles are found in colloidal solutions of mastic, gamboge,  $As_2S_3$ , sulphur, gelatine, fresh solutions of  $ZrO_2$ ,  $CeO_2$ ,  $ThO_2$ .

Needle-shaped particles in sols of  $V_2O_5$ , benzopurpurine and a number of other dyestuffs and of mercurisulfosalicylic acid.

Plate-like particles in sufficiently aged colloidal solutions of  $Fe_2O_3$  (prepared by hydrolysing  $FeCl_3$  solutions), most likely in those of  $Al_2O_3$  and  $CuO$ .

Sometimes phenomena of a more special kind extend our knowledge of the shape of the particles. In concentrated sols with non-spherical particles, the particles have a tendency to arrange themselves in cloud-like clusters as was shown especially by Zocher.<sup>13</sup> In sols with needle-shaped particles as in the colloidal solutions of  $V_2O_5$  or of benzopurpurine, they gather in flame-like groups. Using the ultramicroscope with the azimuth diaphragm it may be seen how the particles lie parallel to one another in these clusters still showing a weak scintillation because of their Brownian movement. These clusters are also visible in the polarisation microscope,<sup>14</sup> for we have here a regular orientation of the particles although the sol is at rest. If the particles are plate-like as is the case in old iron-oxide sols the particles may arrange themselves in parallel layers which are so regular that the light reflected from them has a beautiful iridescent green colour, caused by interference.

In the cases we have considered so far the non-spherical shape of the particles was caused by the fact that the crystals were of a non-regular system or mesomorphous. Cases will now be considered in which the correlation between the shape of the particles and their optical properties on the one hand and the state of aggregation on the other is not so simple. Sols are known which show double refraction although their particles are

<sup>11</sup> O. Wiener, *Abhl. sächs. Akad. Wiss. (Math. Phys. Kl.)*, **32**, 507 (1912).

<sup>12</sup> Frey, *Kolloidchem. Beih.*, **20**, 209 (1925).

<sup>13</sup> Zocher, *Z. anorg. Chem.*, **147**, 91 (1925).

<sup>14</sup> Photographs of such flame-like clusters taken with a polarisation microscope and with an ultramicroscope using the azimuth diaphragm may be found in Freundlich, "New Conceptions in Colloidal Chemistry," p. 98, Figs. 37 and 38.

crystals of the regular system (which do not exhibit double refraction under normal circumstances). Björnstahl<sup>15</sup> has found that gold and silver sols, whose particles give the normal X-ray diagram of the heavy metals and have therefore crystallised in the regular system, show quite noticeable fluxional birefringence and fluxional dichroism. Ambronn<sup>16</sup> noticed many years ago that colloidal gold and silver, that had formed in very narrow spaces between two glass plates or in the pores of fibres was birefringent and dichroitic. A thorough investigation of this case by Berkman, Boehm, and Zöcher<sup>17</sup> gave the following results. An X-ray diagram of ramie fibres dyed with colloidal silver gave a diagram of normal silver crystals in totally irregular distribution next to the spot diagram of the fibres (Fig. 6).<sup>\*</sup> The dichroism and double refraction of the silver could be calculated according to a formula of Wiener<sup>18</sup> assuming a rod-like double refraction of the particles and using the complex index of refraction for massive silver. We therefore have normal silver in these fibres, crystallising in the regular system distributed irregularly in the pores of the fibres in very fine crystals of a rod-like shape. The same held for the case of these fibres containing colloidal gold. Since the double refraction and dichroism of colloidal solutions of these metals in water behave exactly like the double refraction and dichroism of fibres containing these metals, it follows that these sols also contain the metals in a rod-like shape. In this case the fluxional double refraction is not caused by the fact that the crystals are themselves birefringent, because they belong to a non-regular system of crystals, but we have a rod-like double refraction caused by optically isotropic particles of an elongated shape. Why the particles in all these cases form in such irregular shape is unknown; the velocity of crystallisation and the sensibility to small amounts of impurities influencing the growth of different crystal-surfaces in a different way is most likely instrumental in causing this phenomenon.

I pass now to a case where quite different conditions cause the non-spherical shape of the particles. It has been known for some time that rubber latex contains particles of an extraordinary shape. The particles in the latex are not colloidal throughout, a certain fraction of them having dimensions larger than ultramicroscopic. They have a length up to 2 to 4  $\mu$  and are therefore visible under the microscope. Now the particles in the latex of the most important rubber tree, *Hevea brasiliensis*, are mostly pear-shaped. That the smaller particles also are not truly spherical follows from the fact that they show marked scintillations, when viewed under the cardioid ultramicroscope with an azimuth diaphragm. But these particles do not look like crystals, they look like drops which would assume a spherical shape if not prevented by a tough exterior skin. The existence of such a skin has been shown by using a so-called micromanipulator, a micro-dissection apparatus.<sup>19</sup> This instrument may be used in colloidal chemistry for many purposes. It consists of very fine glass needles whose points are not thicker than 0.5  $\mu$ . They are moved by fine screws under the microscope. If the particles of latex are embedded in a suitable gel which prevents the latex from evaporating they may be examined with these micro-dissection needles. It turned out that the interior of the particles

<sup>15</sup> Björnstahl, "The accidental double refraction in colloids," *Diss. Upsala*, 1924.

<sup>16</sup> Ambronn, *Z. wiss. Mikroskopie*, **22**, 349 (1905).

<sup>17</sup> Sophie Berkman, Boehm, and Zöcher, *Z. physikal. Chem.*, **124**, 83 (1926).

<sup>18</sup> O. Wiener, *Kolloidchem. Beih.*, Ambronn, *Festschr.*, p. 89 (1926).

<sup>19</sup> Hauser, *J. R. F.*, **68**, 19, 725 (1924). Freundlich and Hauser, *Zsigmondy-Festschr. Erg. Bd. d. Kolloid. Z.*, **36**, 15 (1925). \* Facing p. 622.

behaved like a stiff fluid perhaps of the consistency of honey. The exterior of the articles behaved like a harder skin. The difference between the interior of the particles and the outer skin was especially marked if benzene was introduced into the particles by means of the micromanipulator and a micropipette. The interior of the particles became less viscous and ran out of the skin and the skin stuck to the needle. The entire character of the skin, its refraction and its behaviour towards organic liquids, prove that it consists of hydrocarbons similar to the interior of the particles.

Pummerer<sup>20</sup> was able to show that it is possible by chemical means to separate out of latex a group of hydrocarbons easily soluble in organic liquids and similar, in behaviour, to the interior of the particles, as well as another group of hydrocarbons which are difficultly soluble and more like the outside skin. The existence of a two-phase system of very closely related substances also seems to follow from experiments by Katz.<sup>21</sup> He found that stretched india-rubber gives an X-ray diagram with dark spots, whereas unstretched rubber has an amorphous diagram. This may be explained on the assumption that crystals of hydrocarbons which are in a state of turgescence in the normal state—the liquid causing turgescence being the other group of hydrocarbons—are made to deturgesce by stretching and are orientated as in fibres.

I finally should like to point out that we know of colloidal systems which contain particles of a still more complicated shape, for instance particles which are helical. If thin layers of a photochloride are exposed to circularly polarised light, they get optically active, as was first shown by Zocher and Coper.<sup>22</sup> This optical activity can only be explained by assuming the existence of colloidal particles of silver of a helical shape. The behaviour of some optically active esters of glycerine in organic solvents also leads to the assumption that these solutions contain colloidal particles, which are screw-shaped.<sup>23</sup>

Passing now from the structure of colloidal particles, I would like to discuss some questions concerning the conditions of their formation. According to Haber,<sup>24</sup> the factors influencing the velocity of the formation of the particles decide their state of aggregation and therefore also their crystalline form and shape. There appears to be a competition between a grouping velocity and an orientation velocity. If the period of precipitate formation is very short, a sufficient time does not elapse for a definite orientation of the molecules to take place. The molecules remain in a state of disorder and the precipitate is amorphous. If, on the other hand, there is a longer time of formation, the process of orientation takes place and the particles are crystalline. One example is perhaps sufficient.<sup>25</sup> A colloidal solution of  $\text{Al}_2\text{O}_3$  may be prepared by a method of Willstaetter<sup>26</sup> by pouring a boiling solution of  $\text{Al}_2(\text{SO}_4)_3$  into a solution of  $\text{NH}_3$ , heating the mixture, washing the rapidly formed precipitate of  $\text{Al}(\text{OH})_3$ , and peptising it with a solution of dilute  $\text{HCl}$ -acid. The colloidal solution is not birefringent when prepared in this way, nor if electrolytes are added; the particles are hence not

<sup>20</sup> Pummerer, *Kautschuk*, p. 85 (1926). Pummerer and Pahl, *Ber.*, **60**, 2152 (1927).

<sup>21</sup> Katz, *Chem. Z.*, **49**, 353 (1925); *Naturwiss.*, **13**, 411 (1925); *Kolloid. Z.*, **36**, 300 (1925); **37**, 19 (1925); see also Hauser and Mark, *Kolloidchem. Beih.* **22**, 63 (1926); *ibid.*, *Ambrosi, Festschrift*, p. 64 (1926).

<sup>22</sup> Zocher and Coper, *Sitzber. Preuss. Akad. Wiss.*, **23**, 426 (1925).

<sup>23</sup> Gruen and Limpacher, *Ber.*, **60**, 255 (1927); see also Freundlich, *Protoplasma*, **2**, 278 (1927).

<sup>24</sup> Haber, *Ber.*, **55**, 1717 (1922).

<sup>25</sup> Aschenbrenner, *Z. physikal. Chem.*, **127**, 415 (1927).

<sup>26</sup> Willstaetter and Kraut, *Ber.*, **56**, 149 (1923).

crystalline, or at any rate are much too small to show phenomena correlated with a crystalline structure. A very distinct fluxional birefringence is found on the other hand in  $Al_2O_3$ -sols, prepared by the method of Crum, if they are sufficiently concentrated or if electrolytes are added to more dilute sols. The particles of this sol are formed very slowly in the course of 6 to 8 weeks by hydrolysing Al-acetate and evaporating the acetic acid. Under these circumstances, the orientation velocity outweighs the grouping velocity and crystalline particles of sufficient length are formed.

Such behaviour is only found when the velocity of crystallisation is sufficiently small. If it is very high it may happen, even if the precipitation proceeds as rapidly as possible, that the particles formed are nevertheless crystalline. This is the case, for instance, in the colloidal solutions of metals such as gold and silver. Particles of these sols always show the X-ray diagram of the heavy crystalline metals, because the velocity of crystallisation is so great. But by a method of precipitation which was extremely rapid and under conditions of utmost dilution Bogdandy, Boehm, and Polanyi<sup>27</sup> were able to prepare a precipitate of silver that gave an amorphous X-ray diagram. They used a metal cylinder rotating in a high vacuum (Fig. 7), the cylinder was hollow and filled with liquid air; its surface had a temperature of about  $-190^\circ$ . Two molecular beams were directed against the surface of the cylinder, one of silver and one of naphthalene. In this way a very close mixture of silver and naphthalene is formed and the silver-powder which is left as residue after dissolving the naphthalene shows an amorphous X-ray diagram (Fig. 8a). If it is heated on the water-bath, it starts glowing and crystallises (Fig. 8b). Under these conditions the grouping velocity is sufficiently high to surpass the very high crystallisation velocity of the silver atoms.

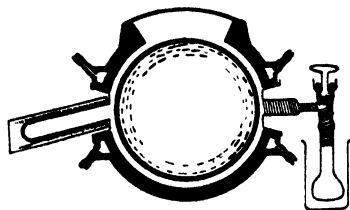


FIG. 7.

On the other hand if the velocity of crystallisation is very small, amorphous particles are found although the precipitation proceeds slowly. This is the case, for instance, for colloidal solutions of  $CeO_2$ ,  $ZrO_2$  and  $ThO_2$ .

The changes which the colloidal particles suffer after their formation are also very manifold and decisive for the behaviour of the sol. In the case of the  $V_2O_5$  sol for instance, the particles of the freshly prepared sol are generally too small to show orientation in flowing, and the sol is therefore without fluxional birefringence. But the particles grow in course of time and the fluxional birefringence appears and gets stronger and stronger. This growth of the  $V_2O_5$  particles is a process of crystallisation.<sup>28</sup> Electrolytes do not influence this change in any marked degree, but other foreign substances do so very strongly; arsenic acid for instance in very small amounts retards the rate of this change. The cause is an adsorption of the arsenic acid on the surface of the particles of  $V_2O_5$ , whereby we have an example of the well-known phenomenon, that impurities adsorbed on a surface strongly retard the velocity of crystallisation.

<sup>27</sup> V. Bogdandy, Boehm, and Polanyi, *Z. Physik.*, **40**, 211 (1926).

<sup>28</sup> Freundlich, Stapelfeldt, and Zocher, *Z. physikal. Chem.*, **114**, 161 (1924).

Freundlich and Dannenberg, *Z. physikal. Chem.*, **119**, 87 (1926).

In other cases, the change found was not caused by crystallisation but by coagulation, as in the cases of the sols of  $\text{Al}_2\text{O}_3$  and of benzopurpurine. An  $\text{Al}_2\text{O}_3$  sol prepared after the method of Crum does not show fluxional birefringence when sufficiently dilute. But if electrolytes are added the fluxional birefringence appears and the different ions behave exactly as is known for the phenomenon of coagulation: since the  $\text{Al}_2\text{O}_3$  sol is positive, the anions are of greatest influence and their influence is correlated with their valency and their adsorbability.<sup>25</sup> The same holds for the sol of benzopurpurine, with this difference that, as this sol is negative, the cations, their valency and adsorbability, are of main importance.<sup>26</sup>

The solutions of mercurisulfosalicylic acid<sup>2</sup> provide a third type of sol with a strong fluxional birefringence. They are not hydrophobic as the sols mentioned so far, but distinctly hydrophilic; indeed they seem to belong to the class of colloids which McBain has called colloidal electrolytes: they behave like soap solutions, a fraction of the acid is in true solution, another fraction forms larger complexes with colloidal properties. The fluxional birefringence depends mainly on the amount of colloidal acid; it diminishes with rising temperature because the amount of colloids diminishes, it rises with lower temperature because the amount of colloid increases. Practically no tendency such as in coagulating electrolytes can be noticed; a tendency towards crystallisation is perhaps extant, but it is not strong.

I should like to conclude with a bird's-eye view of the development of our knowledge about the structure of colloidal particles, choosing as example the colloidal solutions of iron oxide prepared by hydrolysing iron chloride solutions. Péan de St. Gilles,<sup>30</sup> who was the first to investigate them in 1855, spoke of them as watery solutions of an allotropic soluble form of iron oxide. Graham found in 1861, that they had all the signs of those solutions which he had characterised as colloidal; but he would not have been able to say anything about the structure, shape, and magnitude of the particles contained in these solutions. When Majorana<sup>31</sup> discovered in 1902 the surprising birefringence in the magnetic field, shown by these colloidal solutions, it became clear—as was emphasised very soon by Schmauss<sup>32</sup> and by Cotton and Mouton<sup>33</sup>—that the particles of these solutions were asymmetrical; most likely small crystals with a distinct elongated axis. In 1915 it was found<sup>7</sup> that these sols, when sufficiently old, also showed fluxional birefringence and were so similar to the sols of  $\text{V}_2\text{O}_5$ , that an asymmetrical shape of the particles was not to be doubted. X-ray diagrams, measured by Boehm<sup>34</sup> in 1925, made it certain that the particles were crystalline, furthermore that the chemical substance of the majority of particles was a basic iron chloride; but that in old sols there also were particles of rhombic goethite  $\text{FeO}(\text{OH})$ . The behaviour of the Tyndall-light in flowing sols made it very probable that the particles were plate-like.<sup>9</sup> This was confirmed by experiences of Zocher.<sup>13</sup> He found, as was mentioned before, in an old and concentrated iron oxide sol, particles of goethite which were orientated in regular layers strictly parallel to the bottom of the glass-vessel. These layers consisted of plates orientated so regularly, that the light reflected by them showed a beautiful iridescent green colour caused by interference. As also was mentioned before, these layers are caused by

<sup>25</sup> Freundlich and Dannenberg, *Z. physikal. Chem.*, **119**, 96 (1926).

<sup>30</sup> Péan de St. Gilles, *C.R.*, **40**, 568, 1243 (1855); *Y. prakt. Chem.*, **66**, 137 (1855).

<sup>31</sup> Majorana, *Rend. Accad. Linc.*, **11**, I., 536, 539 (1902); **12**, I., 90, 139 (1902).

<sup>32</sup> Schmauss, *Ann. Physik*, (4), **10**, 658 (1903); **12**, 186 (1903).

<sup>33</sup> Cotton and Mouton, *Ann. Chim. Physique*, **11**, 145, 289 (1907).

<sup>34</sup> Boehm, *Z. anorg. Chem.*, **149**, 203, (1925).

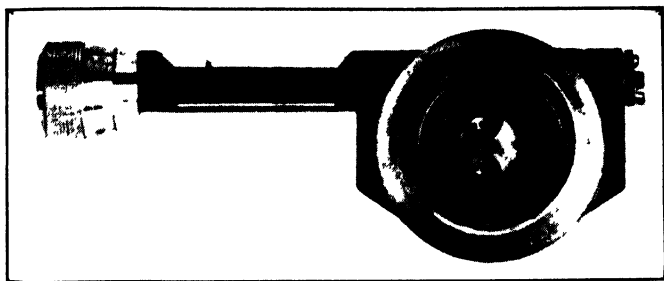


FIG. 2.

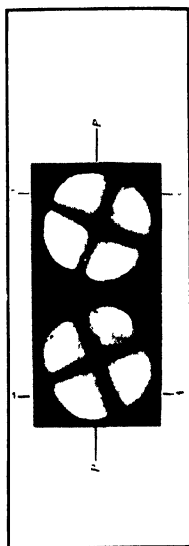


FIG. 5

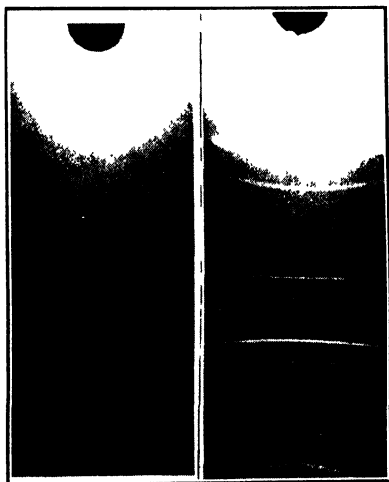


FIG. 8a.

FIG. 8b.

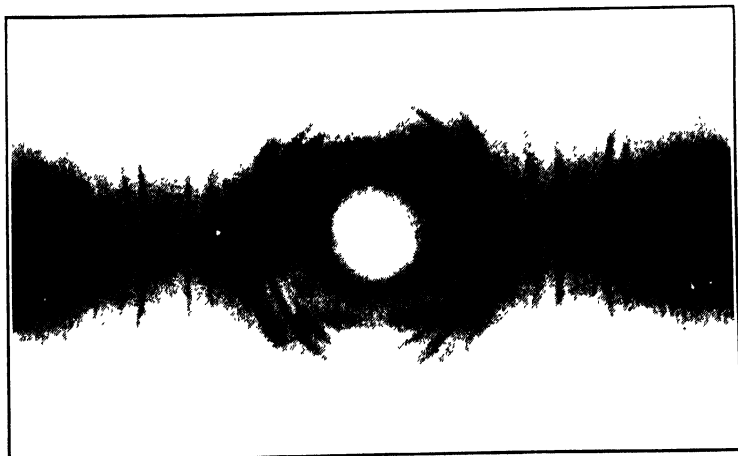


FIG. 6.

[To face p. 622.

(Fells and Firth)

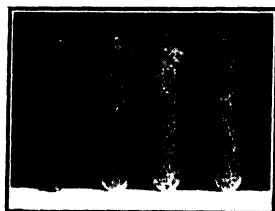


FIG. 1.

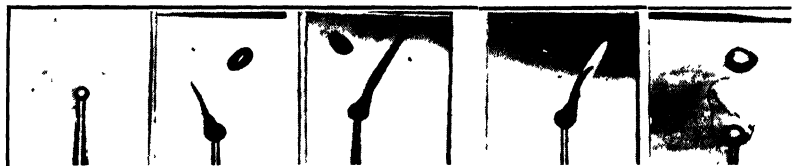


FIG. 4a.

FIG. 4b.

FIG. 4c.

FIG. 5a.

FIG. 5b.



FIG. 7a.

FIG. 7b.

FIG. 7c.

FIG. 7d.

FIG. 7e.



FIG. 8.

FIG. 9.

FIG. 10.

FIG. 11.

(Two positions of same bubble.)

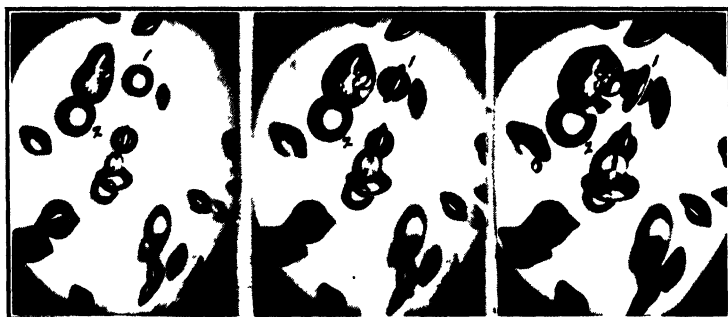


FIG. 12a.

FIG. 12b.

FIG. 12c.

the same factors as the flamelike clusters in the colloidal solutions of  $V_2O_5$ . The layers may be destroyed by shaking up the fluid, but they form again in the course of hours or days. They may be destroyed irreversibly by coagulation with electrolytes. The iridescent colour then becomes irregular and passes through the blue and violet of the second order and the red, yellow and green of the first order until it reaches the bluish-green of the first order. It is even possible to decide the special crystal structure of these plates of  $FeO(OH)$ .<sup>35</sup> If the layers are moved carefully by gentle flowing of the liquid or through the influence of a magnetic field, the plates of each single layer are orientated still more regularly than they were originally, and fluxional birefringence and dichroism as caused. The fluxional birefringence for instance is just as if the vector of the more refrangible ray were parallel to the longer edge of the plate, this lying parallel to the lines of flow. Such a birefringence would be found, if the median line of these rhombic crystals were lying in the plane of the plates. On some kinds of fibrous red iron ore quite similar lamellae also showing beautiful iridescent colours are found.

I believe that the questions I have discussed may prove to be useful especially in laying the foundation for a new morphology of biological systems.<sup>36</sup>

<sup>35</sup> Unpublished results of Boehm and Zocher.

<sup>36</sup> W. C. Schmidt, *Die Bausteine des Tierkörpers im polarisierten Licht*, Bonn 1924. Ettisch and Szegvari, *Protoplasma*, 1, 214 (1926).

Ettisch and Jochims, *Pflug. Arch.*, 215, 519, (1927).

Freundlich, *Protoplasma*, 2, 278 (1927).

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## GELATION OF SILICIC ACID. THE FORMATION OF GAS BUBBLES AND DROPS IN SILICIC ACID DURING GELATION.

BY H. A. FELS AND J. B. FIRTH.

*Received 17th September, 1927.*

In a previous paper the authors described experiments which show that when hydrogen peroxide is added to the sol of silicic acid (prepared by adding sodium silicate solution to hydrochloric acid solution),<sup>1</sup> there is no apparent action. The mixture behaves as a normal gel mixture until a few minutes before setting. Just before gelation, streams of tiny bubbles appear from many points. The viscosity of the mixture changes rapidly near the setting point, and the movement of the bubbles is correspondingly retarded and in a very few minutes the bubbles become fixed, a condition which is coincident with the setting of the gel. The bubbles thus formed are quite small and spherical, but soon begin to increase in size and number. The general appearance of the gel at four stages is shown in Fig. 1.

The authors have shown that<sup>2</sup> the first formed spherical bubbles develop at first by the production of a lenticular belt, passing gradually into flat disc-like bubbles, which become distorted, bending in many planes; subsequently many of the bubbles merge into one another, causing the gel to become broken up into small pieces.

<sup>1</sup> Vide, *γ. physical Chem.*, 29, 241, 1925.

<sup>2</sup> *Proc. Roy. Soc., A*, 114, 517, 1927.

Hatschek<sup>3</sup> produced bubbles of carbon dioxide in gelatine by the decomposition of small amounts of carbonate whilst Harden<sup>4</sup> produced bubbles by fermentation within the gel.

It appeared to the authors that methods for obtaining bubbles within the gel by chemical, catalytic, or enzyme action, have the disadvantage that there is little or no control over the rate of development of the bubble. Thus, in the case of the effect of the addition of hydrogen peroxide to the gel mixture any subsequent development of the first formed spherical bubble is characterised by the formation of a sharply defined belt.

The form taken up by the bubble during development will be primarily dependent on two factors—the rate of increase in volume of the gas, and the rate of change of the medium in which the bubble develops. If the former is very slow relative to the latter during any particular interval, then some changes in gel structure are not indicated during the subsequent development of the bubbles. On the other hand if a bubble could be produced and developed under control it might be possible to show a sequence of changes which under conditions previously adopted (uncontrolled) would not be indicated.

It was with the object of tracing as completely as possible the changes during the setting and ageing of silicic acid gel that the following experiments were devised.

### Experimental.

Gas bubbles were produced by two methods: (1) Electrolysis, (2) blowing air into the medium through a jet. In order to generalise the phenomena, a further series of experiments was carried out in which drops of non-miscible liquids were introduced into the medium by means of a dropping pipette. Two liquids, mercury and chloroform, were used.

In the case of the electrolytic method it was only possible to control the gas-bubble formation to a limited extent, but in the cases of blowing air bubbles from a jet, or the formation of liquid drops, it was possible to produce a single bubble or drop, at any particular stage of gelation and to develop it (if required) after any given interval. It was further possible to produce a single bubble or drop of a composite nature showing the several stages of gelation.

The details of each series are recorded below:—

(1) *Electrolysis of the Solution.*—A rectangular glass tank was filled with a solution prepared by adding water glass, density 1.178, to an equal volume of hydrochloric acid, density 1.121. Two platinum electrodes were submerged in this (Fig. 2), in such a way that the gas bubbles produced on one electrode would rise through the main portion of the solution. A fairly large volume of gas accumulated on the electrode before a portion was released as a bubble. The first bubbles released were spherical and rose vertically to the surface.

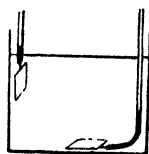


FIG. 2.

These spherical bubbles were formed for a considerable time, but very gradually they changed their shape. As the viscosity increased, the bubbles assumed an elongated shape as soon as they formed. The tendency to become elongated became more pronounced as the setting point was approached, until finally, very flat disc-like bubbles only were formed. These did not rise vertically, but usually took an oblique path to the surface. Once a bubble had passed to the surface, all the subsequent

<sup>3</sup> Koll. Z., 15, 228, 1914.

<sup>4</sup> Vide, 3.

bubbles followed the same path. Although by this method bubbles could be produced at any desired stage, the control over the rate of development was limited. It is of interest, however, as a method of bubble formation in silicic acid gel, quite distinct from those previously adopted.

(2) *The Blowing of Air-bubbles Through a Jet.*—(a) A silicic acid sol was prepared, as described in 1, and put in a glass vessel through the base of which passed a fine jet, having an orifice as truly circular as possible. Air could be blown through the solution from the jet by means of a compressed volume of air regulated by a tap. It was thus possible to blow a bubble at any moment, and to have only one bubble in the solution under observation.

Exactly similar results were obtained by this method as by method 1, but the changes in shape could be more easily followed. These changes in shape of the first series of bubbles however could not be photographed, as the bubbles once released from the jet passed through the solution too quickly, and so the method of their production had to be modified. A series of diagrams (Fig. 3) will serve to show the gradual change in the shape of the bubble passing through the gel from the time of mixing to the final setting of the gel. The final setting of the gel was indicated by the formation of disc-like bubbles. Once the gel had set no further changes

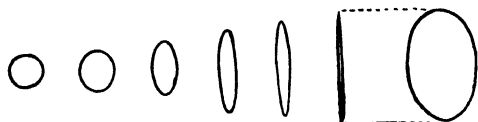


FIG. 3.

could be observed. All subsequent bubbles took the same shape and escaped along the same path (see p. 628).

(b) *Modified Method.*—Instead of allowing the first bubble to release itself from the jet, it was blown so that it remained attached to the jet as a spherical bubble. At intervals of five minutes, the volume of the bubble was increased and the following results were obtained. The enlargement of the first bubble did not give a larger spherical form, but a wing-like extension was produced, and each subsequent enlargement resulted in this outgrowth becoming more extended in distinct stages. At each stage, the "wing" became much thinner, so that finally a composite bubble was formed, showing as many stages as intervals of time passed.

These results can be clearly seen in Figs. 4 and 5. With a solution which required a longer time for gelation, the same type of composite bubble was formed, but each stage was not so well defined. Two other important features were observed during these experiments.

1. If a bubble were produced during the early history of the solution, it assumed a certain form dependent upon the conditions at the moment of its formation. If this bubble were allowed to remain stationary in the medium, until the gelation was complete, it underwent *no change in shape*.

2. If a composite bubble were produced on the end of the jet, the air could easily be withdrawn from it and the bubble would completely disappear. On re-admitting the air, the bubble *assumed its former shape*.

*Pressure Required to Blow the Bubbles.*—A simple manometer was introduced into the air delivery system and the pressure record shown by the manometer, was magnified by a lever attachment, which in turn made a continuous record on a revolving drum. As air was admitted the pressure gradually rose during the formation of the bubble until the bubble escaped

from the jet, at which instant the pressure suddenly fell and, then, gradually increased again during the formation of the next bubble. A typical series of results is recorded in Table I.

TABLE I.

No. of Reading.	Pressure to Blow Bubble in Mm.	Pressure after Bubble Escapes.	Time in Seconds after First Bubble.
1	1.77	0	(20 mins. after mixing)
2	2.95	0	35
3	4.13	0	89
4	4.72	0	129
5	5.31	0	319
6	5.34	0.59	344
7	5.9	1.77	394
8	6.49	2.36	534
9	6.49	2.95	672
10	6.49	4.72	808
11	6.49	5.31	946
12	7.08	5.41	1080
13	54.00	0	(24 hours)

A mixture was prepared of equal volumes of hydrochloric acid  $\Delta 1.121$ , and sodium silicate solution  $\Delta 1.178$ . The pressure required to just keep the jet clear of liquid was taken as zero throughout. The first observation was made 20 minutes after mixing. It will be observed from the table that the maximum pressure developed for this first bubble was 1.77 mm. and when the bubble escaped from the jet, the pressure returned to zero. The pressure required to blow the next four bubbles showed a continuous increase, and in each case the pressure returned to zero. In all subsequent attempts to blow and release a bubble, the bubble was only partially released, and a residual pressure therefore remained. This residual pressure continuously increased as the gel aged.

It has been shown (p. 625) that once a bubble has been formed it produces a kind of mould, such that the air, (or liquid) can be withdrawn and returned at will, the identical form of the bubble being re-assumed. It will be apparent therefore that any increase in pressure will be that required to produce an enlargement of the bubble. Owing to the peculiar shape of the later expansion of the bubble the internal forces act unequally on the walls, with the result that there is always a tendency for the last segment to break away (*i.e.* to break away at the junction *a* in Fig. 6).



FIG. 6.

As the last segment approaches film-like dimensions this phenomenon becomes more pronounced, and ultimately it is mainly the last film-like extension which is released.

The results show clearly the gradual and continuous increase in the cohesive forces within the gel. Finally a passage of air through the gel can only be obtained by the application of a considerable pressure (54 mm.), which produces a permanent rupture from the jet to the surface. The fracture produced is usually conchoidal in character.

The significance of the foregoing observations will be discussed after an account has been given of the experiments with liquid drops in the gel.

3. *The Formation of Chloroform Drops.*—Chloroform, in which iodine was dissolved so that the drops could be easily seen, was allowed to run from a narrow jet into a solution of water glass and hydrochloric acid.

Water-glass of density 1.180, and hydrochloric acid of density 1.142 were used in equal volumes.

When the mixture was freshly prepared, the drops of chloroform were spherical, and sank to the bottom. As the viscosity increased, the drops required a longer time to reach the bottom, but remained spherical. After this stage a drop could be formed which did not sink to the bottom, but remained suspended in the gel. The drops now assumed an ovate form, and beyond this point the chloroform tended no longer to fall, but to rise to the surface round the jet.

Attempts were then made to produce a composite drop. A spherical drop of chloroform was suspended from the jet and more chloroform was run into it at intervals of five minutes. The drop increased in size just as in the case of the air bubble. The similarity of the composite drop and composite bubble will be seen by comparing Figs. 7 and 4.

In a further experiment with chloroform, a drop was allowed to remain suspended in the gel until a well marked stage had been reached in the process of gelation, and the tube was then immersed in hot water. This caused the chloroform to be vapourised, but instead of the spherical drop increasing uniformly in size, the gas escaped as a very thin film, making a path for itself towards the surface. When all the chloroform had been vapourised, the skeleton of the drop remained, the original spherical shape with a very thin film protruding from it (Fig. 8).

4. *The Formation of Mercury Drops.*—Mercury was dropped into a silicic acid medium as in Method 3 and, again, the primarily formed drops were spherical. The usual series of changes in shape was observed again, but the earlier stages were difficult to see, as the drops of mercury sank to the bottom very quickly. With the later stages, however, the very flat disc-like drops took an oblique course and, consequently, they were fixed in approximately a horizontal position. A few were actually fixed as flat discs in a vertical position (Fig. 9). Fig. 10 shows a disc of mercury which was produced in a horizontal position, but owing to the mobility and high density of the mercury, a well marked plane was made by it in which it was free to move. This plane was clearly marked from the rest of the gel as it was more transparent and apparently was filled with a watery liquid.

A curious but interesting modification of this production of a clear-looking plane of cleavage can be seen in Fig. 11. A drop of mercury was allowed to fall through a gel before gelation had proceeded very far and, instead of dropping obliquely, a spiral path was taken. The shape of the containing vessel probably affected the ordinary oblique path which would have been taken had the body of the gel been sufficiently large. The spiral path taken by the drop was not at first very noticeable, but the same path was taken by all subsequent drops. After standing for about 12 days, this path became very clearly marked, being far less opaque than the rest of the gel, and containing a watery fluid. (See Fig. 11).

It will be apparent from the foregoing experiment that the shape of a bubble or drop is determined by the stage which has been reached in the medium at the instant of the bubble or drop formation. When certain conditions in the medium are attained the gel "sets." Does this take place uniformly throughout the entire mass at the same instant or are some portions of the medium "not gelled"?

It had been previously observed that, in the formation of bubbles by the decomposition of hydrogen peroxide,<sup>2</sup> the *number* of bubbles increased *after* gelation. In the light of the foregoing experiments it would appear that if the setting of the gel takes place uniformly throughout, then any

bubbles formed after the first formed bubbles had begun to develop a lenticular belt, should be lenticular.

A silicic acid medium to which hydrogen peroxide solution had been added was prepared as previously described<sup>2</sup> and the development of the gas bubbles carefully observed under the microscope. The observations of a portion of the gel are recorded in photographs in Fig. 12. The photographs were taken at intervals of five minutes. In photograph (a) bubble marked 1 is a spherical bubble, as is shown by the subsequent development of the lenticular belt in (b) and (c). The spherical bubble 1 in (a) was formed after lenticular belts had developed on the bubbles in other portions of the gel. Bubble 2 in (a) is not spherical but its appearance is due to the position of observation as is shown by the corresponding photographs of the same bubble in (b) and (c).

It would appear from these observations that after the initial setting of the gel there are still small portions of medium "ungelled," *i.e.*, gelation is not instantaneous throughout the entire medium.

### Discussion.

In the series of experiments herein described, a continuous record of the several stages of gelation has been obtained.

It has been shown that the bubbles or drops produced in the medium prior to gelation are invariably spherical. Gelation is associated with a change in the shape of the bubble or drop which can be produced. The change, however, is very gradual and the various stages from the spherical to the thin film have been recorded. In fact it is suggested that this change of shape of the bubble or drop may be taken as indicative of gelation. Many authors describe gelation in very vague terms, *e.g.* "When the containing vessel can be turned upside down without the gel falling out."

The character of the bubble gives some indication of the internal condition of the gel. It has also been pointed out that once a bubble or drop was formed in the gel, the shape was permanent, *i.e.* a spherical bubble or drop remained spherical, and further, the air or liquid could be withdrawn and replaced at will. Thus any subsequent development of the bubble or drop appears as a growth on the original bubble or drop.

After gelation, up to the condition for the formation of the extremely thin film-like bubble which brought about a permanent fracture in the gel, the only apparent change in the gel was that of continued increase in rigidity. It was only subsequent to this stage that external syneresis was observed. It has been shown that the pressure required to blow a bubble increases as the gel ages, and that once a bubble passes through the gel, subsequent bubbles follow the same path. After a time this path becomes very pronounced, and bubbles pass along it with comparatively little resistance. It has been further observed that where the path terminates in the surface of the gel, liquid exudes. It would appear therefore that the internal pressure produced by the passage of the first formed bubble has caused syneresis<sup>5</sup> to take place at the point of the bubble formation and along its subsequent path through the gel.

When mercury is used this phenomenon is more pronounced owing to the natural weight of the drop, and this is clearly shown in Figs. 10 and 11.

In a previous communication<sup>6</sup> it has been shown that the water present in the gel is of two types, "fixed" water and "free" water. "The

<sup>2</sup> Cf. O. F. Lenher, *J. Am. Chem. Soc.*, **43**, 391-6, 1921.

<sup>5</sup> *J. physical Chem.*, **31**, 1230-36, 1927.

fixed water is a certain varying amount of the total water in the gel, which is definitely associated with the silica. The 'free' water is the remainder of the total water not acting as 'fixed' water. It is free in the sense that it is only enclosed in the meshes or pores of the gel, or interstices between adjacent hydrated particles. It is capable of acting as solvent for the sodium chloride present and can be easily removed by dessication over sulphuric acid. The 'fixed' water cannot be so easily removed."

When the medium undergoing gelation has almost gelled the amount of water definitely associated with the silica has reached a maximum and the heavily hydrated particles may be represented by the formula



These heavily hydrated particles are still free to move, but the movement is extremely limited as is indicated by the rapid increase in viscosity just prior to gelation. The instant of gelation is the point of maximum hydration and the hydrated silica particles which were originally free to move are now part of a continuous structure, very loose and extended and containing large voids in which the residual free water is enclosed. Then follows a continuous increase in rigidity which is at first fairly rapid. This increase in rigidity is brought about by a continuous change of "fixed" to "free" water, whereby a firmer union between the silica particles results.<sup>6</sup> This change may be represented thus—



where  $a$  is continuously increasing.

It would appear, however, that the foregoing changes do not take place uniformly throughout the medium. It has been shown that in the ungelled medium bubbles and drops invariably take a spherical form, whilst gelation is associated with a change to the lenticular form. On the other hand, the results indicate that whilst lenticular bubbles are produced in the major portion of the gel, there are still sections in which spherical bubbles are formed, *i.e.* even after "general gelation" there exist ungelled portions of the medium. It is suggested that gelation takes place round a series of gelation centres.

The observation of internal syneresis along the path of the bubble or drop, and also when the bubble is withdrawn from the gel, is due to the rupture of what would otherwise be a continuous structure; owing to the comparative rigidity of the gel "free" water rapidly drains into the path or cavity, hence subsequent bubbles are only displacing water (aqueous solution), until the previous state of development has been reached. It would appear, however, that when the bubble is in the nature of a thin film, the surfaces caused by the passage of the bubble come together again so quickly that no syneresis can be discerned, in fact, the film-like bubbles "shoot" through the gel with a distinct "click." Repeated passage of the film, however, finally produces a "syneresis path."

It is not until the gel has reached a stage of rigidity, such that any attempt to blow a bubble produces a permanent fracture, that syneresis at the surface of the gel, accompanied by shrinkage, takes place. The change takes place in such a way, the gel shrinking to such an extent, that the large meshes formed in the semi-rigid gel ultimately become so small in the hard gel as to be of the nature of capillaries.

The hard "dried" friable gel still contains a certain amount of fixed water, very difficult to remove by laboratory methods, which is, however, lost by the influence of time, with the ultimate formation of anhydrous

crystalline silica. The probability of the final production of silica in a crystalline and anhydrous condition was suggested by Zsigmondy,<sup>7</sup> who also showed that the actual crystalline form assumed was that of quartz. This is substantiated by the fact that silicic acid gel was found occurring naturally in the Simplon Tunnel<sup>8</sup> and apparently it was changing gradually into quartz, which was found along with the gel. From a purely theoretical point of view, Arsen's<sup>9</sup> contribution on the tendency to the ultimate formation of a crystal lattice further supports the conception that a process of slow crystallisation is taking place during the ageing of silicic acid gel.

In conclusion, it would appear that the silica gel is always tending to the ultimate formation of crystalline anhydrous silica. This change is accompanied by considerable shrinkage and corresponding expulsion of the free water. It is this tendency of the hydrated silica particles to orientate themselves towards the final production of a crystal lattice, with consequent loss of water, which is responsible for the formation of capillaries in the hard gel.

<sup>7</sup> *Z. anorg. Chem.*, **71**, 336-77, 1911.

<sup>8</sup> *Z. Kryst. Min.*, **34**, 289-90, 1901.

<sup>9</sup> *J. physical Chem.*, **30**, 306, 1926.

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## PERIODIC ANOMALIES IN THE PROPERTIES OF LONG CHAIN COMPOUNDS.

BY W. B. LEE.

(Communicated by PROFESSOR J. W. MCBAIN.)

(Received, 3rd August, 1927.)

It has long been known that many of the physical properties of members of homologous series do not change regularly with increasing molecular weight but show periodic fluctuations. One of the most marked of these is that observed in the melting-points of successive members of an homologous series such as the fatty acids. This problem has been studied extensively and several attempts have been made to explain the phenomenon. Tammann<sup>1</sup> suggested that the acids with an even number of carbon atoms exist in two stable constant forms and, in support of this, showed that acetic acid is dimorphous. Two other types of explanation have also been advanced (1) stereochemical, (2) electronic. The first of these is due to Pauly<sup>2</sup> and Stark<sup>3</sup> and seems to have received confirmation from the later X-ray investigations. It appears to be widely accepted that in long chain compounds such as the fatty acids the carbon atoms are arranged in a kind of "zig-zag" manner. Cuy<sup>4</sup> and others brought forward electronic theories. The first extensive collection of data relating to the alternation of physical properties between the odd and even members of homologous

<sup>1</sup> Tammann, *Z. anorg. Chem.* (1919), **109**, 221-225.

<sup>2</sup> Pauly, *ibid.* (1921), **119**, 271-291.

<sup>3</sup> Stark, *ibid.* (1921), **119**, 292-298.

<sup>4</sup> Cuy, *ibid.* (1921), **115**, 273-287.

series is that of Biach.<sup>5</sup> Garner and Ryder<sup>6</sup> have also added to our knowledge of this subject.

There is, however, another anomaly in the properties of members of certain homologous series which does not seem to have attracted sufficient notice. It will be shown later that periodic irregularities occur when the number of carbon atoms in certain straight chain compounds is five or a multiple of five. On certain stereochemical models one might expect a periodicity at these positions in the chain. In an examination of adhesion phenomena \* the author<sup>7</sup> was struck by the prominence of this anomaly, and in consequence was led to investigate the data for many other physical properties and has found, as is shown in the sequel, that this periodicity is very common.

### The Optically Active Carbinols $C_2H_5 \cdot CHOH \cdot C_nH_{2n} + 1$ .

(1) *Optical Activity*.—Pickard and Kenyon<sup>8</sup> prepared three series of active secondary alcohols, namely, methyl R carbinols, isopropyl R carbinols, and ethyl R carbinols ( $R = \text{alkyl}$ ), with the following results:—

In the methyl series the rotations of the homogeneous liquids increase regularly with the molecular weight; in the isopropyl series they increase rapidly to  $C_4H_9$  and then remain nearly constant. The most interesting series is the ethyl-R-carbinols, where there are sudden increments at the fifth, tenth, and fifteenth carbon *radicals* and also similar but smaller increments when the *whole chain* makes five or a multiple of five carbon atoms. [As the effect is emphasised in alcoholic solution the authors consider that it is important not to restrict observations to homogeneous liquids.]

(2) *Static Friction*.—The above ethyl R carbinols have been studied as lubricants by Miss Doubleday.<sup>9</sup> The static friction on steel and glass was measured. For the most part the data fit the well-known linear relation  $\mu = b - aM$  (Hardy), but a striking exception was found at the carbinol containing 15 carbon atoms in all, together with less notable exceptions at the  $C_4$  and  $C_5$  carbinols. Miss Doubleday ascribed the abnormally high value (for the  $C_{15}$  compound) to impurity, and stated that the other anomalies might be expected.

(3) "*Cohesion*."—Quantitative "adhesion" experiments were made by the author using five of the solid members of the ethyl-R-carbinol series as adhesives between plane or optically plane metal surfaces. The joint-strength tests in tension showed a maximum value at the  $C_{15}$  carbinol; rupture of these joints occurred in the very thin adhesive film itself rather than at the metal-adhesive interface. [The  $C_{13}$ ,  $C_{14}$ ,  $C_{15}$ ,  $C_{16}$ , and  $C_{18}$  carbinols were included in these tests.] . . . McBain and Lee<sup>10</sup> have shown that the normal pull is related to the appropriate static friction. The molecular attractive fields of the opposing metal surfaces appear to modify the properties of the exceedingly thin liquid or subsequently solidified adhesive film.

<sup>5</sup> Biach, *Z. physikal. Chem.*, **50** (1904), 43.

<sup>6</sup> Garner and Ryder, *Trans. Chem. Soc.*, (1925), p. 722.

\* On which I have been engaged with Professor J. W. McBain on behalf of the Adhesive Research Committee of the Department of Scientific and Industrial Research.

<sup>7</sup> Lee, *Nature*, **120**, 48, July 9 (1927).

<sup>8</sup> Pickard and Kenyon, *Trans. Chem. Soc.* (1913), 1924.

<sup>9</sup> Doubleday, *Trans. Chem. Soc.*, **121**, 2875 (1922).

<sup>10</sup> McBain and Lee, *Proc. Roy. Soc., A*, **113**, 619 (1927).

(4) *Density of Molten Adhesive*.—In the series of optically active ethyl-R-carbinols the density of the homogeneous liquid  $D_{40}^0$  passed through a maximum at the fifteenth carbon atom in the whole chain.<sup>8</sup>

### The Normal Saturated Fatty Acids.

(5) *Heat of Crystallisation*.—The heats of crystallisation of normal fatty acids show a marked alternation between the odd and even members as the series is ascended, *but* the heat of crystallisation of the terminal methyl and carboxyl groups changes from a positive to a negative value at  $C_6$ . Garner, Madden, and Rushbrooke<sup>11</sup> give the following values:—

$C_2$	$C_4$	$C_6$	$C_8$	$C_{10}$	$C_{12}$	$C_{14}$	$C_{16}$	$C_{20}$
+2.77	+0.58	-0.52	-1.07	-1.55	-1.55	-1.62	-1.44	-1.59

Characteristic points occur at  $C_6$ ,  $C_{10}$ , and  $C_{14}$  (or,  $C_{16}$ ?)

(6) *Density of Packing of "Monomolecular" Films*.—Harkins<sup>12</sup> gives a table for the number of molecules per sq. cm. in "monomolecular" films of fatty acids on a water surface. He concludes that "as the number of carbon atoms increases up to 16, the number of molecules per unit area increases, and beyond this number falls again." ( $C_{14}$  and  $C_{15}$  chain acids were not included in the table.) Certain of the results were bracketed in Harkin's table, without explanation. Taking these into account maxima occur at  $C_6$  (or  $C_6$ ),  $C_{10}$ , and at about  $C_{15}$ .

(7) *"Surface Pressure" and "Spreading Coefficient"*.—Cary<sup>13</sup> measured the "spreading coefficients" of the normal fatty acids ( $C_{11}$  to  $C_{18}$ ) on a water surface at the melting-point. His results show a maximum value for the equilibrium film pressure at pentadecylic acid ( $C_{15}$ ). The equilibrium pressure appears to be independent of the ordinary fluctuations of melting-point between the odd and even members of the normal fatty acids and it is worth noting that the equilibrium pressure for the fatty acids runs symbatically with the static friction values for the *carbinols* throughout the whole range ( $C_{11}$  to  $C_{18}$ ) over which a comparison can be made. It also runs parallel with the static friction values for the normal fatty acids, but up to  $C_{14}$  only. The finding of Sir William Hardy<sup>14</sup> that static friction is a linear function of molecular weight agrees with the observation that the spreading coefficient or surface pressure is also to a first approximation a linear function of molecular weight up to  $C_{14}$ .

(8) *Temperature at which "Surface Solution" Begins*.—Cary<sup>13</sup> has studied the alteration of the "equilibrium pressure" with temperature for the series of chain acids  $C_{11}$  to  $C_{18}$ . He found that no measurable lowering of the surface tension of the water occurred until a well-defined temperature was reached. On plotting Cary's values for this temperature at which surface solution begins a well-defined irregularity occurs at  $C_{14}$ .  $C_{14}$  corresponds to a maximum and  $C_{15}$  to a well-defined minimum. If instead of plotting as ordinate the temperature at which surface solution begins we plot the corresponding number of degrees below the melting-point of the bulk phase there is then a well-defined minimum at  $C_{14}$  and a maximum at  $C_{15}$ .

(9) *Electrical Properties of Monomolecular Films*.—The electrical properties of monomolecular films of adsorbed insoluble substances were

<sup>11</sup> Garner, Madden, and Rushbrooke, *Trans. Chem. Soc.*, **II** (1926), p. 2497.

<sup>12</sup> Harkins, "Colloid Symposium Monograph," **II**, p. 170.

<sup>13</sup> Cary, *Proc. Roy. Soc., A*, **109**, 318 (1925).

<sup>14</sup> Hardy and Doubleday, *Proc. Roy. Soc., A*, **100**, 549, (1922); *ibid.*, **101**, 487 (1922); *ibid.*, August (1923).

investigated by Frumkin<sup>15</sup> who measured the *P.D.* at the interface air—adsorbed film. Films of fatty acids and allied substances on 0.01 *N.* HCl were studied. The following normal fatty acids were investigated C<sub>7</sub>, C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, C<sub>20</sub>. The maximum electrical effect for all the acids C<sub>7</sub> to C<sub>12</sub> inclusive lay between the limits 320 and 335, which was therefore roughly constant. There is a sharp rise in the curve at myristic acid (C<sub>14</sub>) to 382, followed by 390 and 290 for the C<sub>16</sub> and C<sub>18</sub> chain acids respectively: and the ratio of the *P.D.* to the adsorption is appreciably smaller than for the lower members. This ratio is taken as approximately constant for the members C<sub>7</sub> to C<sub>12</sub> inclusive although between butyric acid (C<sub>4</sub>) and lauric acid (C<sub>12</sub>) Frumkin<sup>15</sup> considers that this ratio probably diminishes by about 10 per cent.

(10) *Solubility*.—N. K. Adam<sup>16</sup> referring to the solubility of mono-molecular films states that “on nearly neutral solutions solubility of the acids up to pentadecylic may be noticeable. Addition of one carbon atom to the chain very much decreases solubility. When the C<sub>15</sub> acid is insoluble and the C<sub>14</sub> film decreases at about 1 per cent. per minute, a film of tridecylic acid will disappear about ten times as fast and the C<sub>12</sub> acid so fast that before any measurement of area can be taken probably about one-third of the film will have disappeared.”

Langmuir<sup>17</sup> gives the following values:—

	Observed Solubility (Mol. Fraction).	Temperature.
C <sub>4</sub> butyric acid . .	0.052	-2°
C <sub>6</sub> valeric acid . .	0.0062	16°
C <sub>8</sub> nonylic acid . .	$1.4 \times 10^{-5}$	25°
C <sub>14</sub> myristic acid . .	$ca. 10^{-8}$	20°

The solubility of myristic acid is exceedingly small.

(11) *Viscosity*.—Dunstan<sup>18</sup> determined the viscosities of the normal saturated fatty acids. He concluded that “the logs. of viscosities plotted against molecular weight give for each temperature an apparently linear curve between the limits C<sub>3</sub> – C<sub>9</sub>. Below this limit there is seen the abnormally high values of the first two members and above it there occurs a steady diminution in the homologous increment. Although the main part of the curve appears to be linear a close inspection of the CH<sub>2</sub> differences shows some irregularity between C<sub>5</sub> and C<sub>6</sub>.” An examination of the data also seems to indicate a definite irregularity in log-viscosity at C<sub>14</sub> (C<sub>15</sub> was not included in the viscosity determinations). [The density data D<sub>4</sub><sup>t</sup> for the fatty acids at 70° and 90° also show a drop (at palmitic acid C<sub>16</sub>) between myristic and stearic acids].

(12) *Magnetic Rotation*.—Perkin<sup>19</sup> studied the magnetic rotatory polarisation of the normal saturated fatty acids (C<sub>3</sub> to C<sub>9</sub>). The molecular rotation increments per CH<sub>2</sub> added to the chain indicate that the rotation is increasing more rapidly at about C<sub>6</sub> and C<sub>9</sub> (or C<sub>10</sub>?). The so-called “series constant” exhibits maxima at C<sub>6</sub> and C<sub>9</sub>. Perkin has also compared the magnetic rotation values of the normal fatty acids (C<sub>4</sub> to C<sub>8</sub>) with those of the corresponding polymethylene monocarboxylic acids containing two atoms

<sup>15</sup> Frumkin, *Z. physikal. Chem.* (1925), **116**, 485.

<sup>16</sup> Adam, *Proc. Roy. Soc., A*, **101**, 467 (1922).

<sup>17</sup> Langmuir, *Colloid Symposium Monograph*, **111**, p. 63.

<sup>18</sup> Dunstan, *Trans. Chem. Soc.*, **107**, 667-72 (1915).

<sup>19</sup> Perkin, *ibid.* (1884).

of hydrogen less. The differences were very irregular and gave a pronounced maximum for the  $C_8$  compounds. Perkin<sup>20</sup> (*l.c.*) obtained more constant differences by regarding the tri- and tetra-methylene compounds as analogous to the first two members in the aliphatic series and in this case the greatest difference corresponded to the  $C_5$  chain acid.

(13) *Dissociation Constants*.—The following table gives the dissociation constants of the lower normal fatty acids at 25°:—

	Ostwald.	Jahn.	Franke.	Salm.	Dhar and Datta.
Formic 10 <sup>5</sup> K .	21·4	—	21·4	22·0	24·0
Acetic 10 <sup>5</sup> K .	1·8	1·85	1·8	1·85	1·95
Propionic 10 <sup>5</sup> K .	1·34	1·42	1·34	1·4	1·33
Butyric 10 <sup>5</sup> K .	1·49	1·69	1·52	1·7	1·55
Valeric 10 <sup>5</sup> K .	1·61	1·77	1·5	1·75	—
Caproic 10 <sup>5</sup> K .	1·45	—	—	—	—

Ostwald's values show that the curve connecting the dissociation constant with molecular weight gives a maximum at the  $C_5$  chain acid and the other data also lend support to this view.

(14) *Heat of Neutralisation*.—Ostwald<sup>21</sup> gives the following table:—

Formic acid . . . . .	134 K.
Acetic acid . . . . .	133 K.
Propionic acid . . . . .	134 K.
Valeric acid . . . . .	140 K.

The highest value is obtained with the  $C_5$  chain acid.

(15) *Heat of Combustion*.—Stohmann<sup>22</sup> determined the heats of combustion of the normal fatty acids ( $C_1$  to  $C_6$ ,  $C_8$ ,  $C_{10}$ ,  $C_{12}$ ,  $C_{14}$ ,  $C_{16}$  (solid),  $C_{18}$  (solid)). The increments in the heat of combustion of gram-molecular weights per  $CH_2$  added are very nearly constant, but a pronounced minimum occurs between  $C_{14}$  and  $C_{16}$  followed by the highest increment of the whole series between  $C_{16}$  and  $C_{18}$ . [There are also indications of an irregularity in the heat of combustion of the hydrocarbons of the methane series at  $C_5$ .]

(16) *Esterification Constants*.—Sudborough and Gittins<sup>23</sup> give the following values:—

	$K_{McOH}^{15^\circ}$	
Formic . . .	1124	The authors ( <i>l.c.</i> p. 217) state that "the values obtained for decolic acid ( $C_{10}$ ) show that the constant tends to decrease with the concentration of the acid more markedly than with other acids, but the cause of this we have not been able to determine."
Acetic . . .	104	
Propionic . . .	91·9	Their results lend support to the view that peculiar changes occur at $C_8$ , $C_{10}$ , and $C_{14}$ (or $C_{18}$ ?). Other work by Sudborough <sup>23</sup> on esterification leads to minimum values at caproic, decolic, and myristic acids.
Butyric . . .	50·0	
Valeric . . .	53·5	
Hexoic . . .	51·5	
Heptoic . . .	52·5	
Octoic . . .	54·6	
Nonoic . . .	53·6	
Decoic . . .	51·8	
Lauric . . .	52·9	
Myristic . . .	52·9	
Palmitic . . .	49·7	
Stearic . . .	53·7	

<sup>20</sup> Perkin, *Trans. Chem. Soc.* (1902), p. 293.

<sup>21</sup> Ostwald ("Outlines General Chemistry," p. 120).

<sup>22</sup> Stohmann (*cf.* Ostwald's "Outlines," p. 242).

<sup>23</sup> Sudborough and Gittins, *Trans. Chem. Soc.* (1908), p. 211; *Chem. Zentralblatt* (1926) 1, 80.

(17) *Smell-Strength*.<sup>24</sup>—The critical distance for the "odoroscopic charging phenomenon" and the log. of the "mol. smell-strength" when plotted against molecular weight give curves of similar shape in the alcohol series, but with the fatty acids the "smell-strength" shows a maximum with valeric acid ( $C_5$ ), the "central distance" with caproic acid ( $C_6$ ).

(18) *Toxicity ("Contact Insecticides")*.—"For the fatty acids toxicity increases on ascending the series up to  $C_{11}$ , after which there is a decline. Toxicity disappears at myristic acid ( $C_{14}$ )."<sup>25</sup> "An analysis was made of the bearing of certain physical properties on the toxicity of fatty acids. None of these, however, were found to account fully for the values obtained." (See abstract of paper by Tattersfield and Gimingham.<sup>25</sup>)

Siegler and Popenoe<sup>26</sup> found that the lower saturated monocarboxylic acids have no marked toxicity to insects, but the higher members are decidedly toxic. Practical toxicity begins with caproic acid ( $C_6$ ). Caprylic, capric, and lauric acids and to a lesser extent myristic acid are toxic. Nonoic is about equal to lauric.

(19) *Induced Double Refraction*.—Vorlander and Walter<sup>27</sup> have studied the mechanically-enforced double refraction of amorphous liquids in relation to molecular configuration. There is some connection between the optical properties and length of carbon chain. With increasing number of carbon atoms the values for the "specific double refraction" of fatty acids increase at first slowly, then very rapidly, and finally become nearly constant. The steep portion of the curve (normal fatty acids) begins at  $C_4$  or  $C_5$  and ends at  $C_9$  or  $C_{10}$ . The glycerides of the fatty acids behave similarly, but the curve here rises much more slowly; nevertheless there is an apparent break in the curve at or near tributyrin.

(20) *Heat of Wetting*.—Gurvich<sup>28</sup> finds that oxygen compounds have a greater heat of wetting with, and are also adsorbed more by adsorbents containing oxygen compounds or are "oxophil," while hydrocarbon compounds are more attracted by charcoal or are "carbophil." With increase of molecular weight of a series, the oxophil effect of oxygen decreases to a minimum at about  $C_5$ ; the attractive force increases again because of increase in weight.

(21) *Partition Coefficients and Nernst's "n."*—The distribution of the first six normal fatty acids between benzene and water at 25° has been measured by Brown and Bury<sup>29</sup> with the object of determining how this varies from member to member of a homologous series. When the concentration of acid in the benzene layer is less than about 0.75*N*, the results are best represented by the Nernst formula  $\frac{C_w^n}{C_b} = k$ . The authors found

that the index  $n$  increases irregularly with the number of carbon atoms. There is a minimum at  $C_4$  followed by a sharp rise at  $C_5$ .

(22) *Foam-Stability*.—Bartsch<sup>30</sup> found pronounced irregularities at the  $C_6$  normal alcohol and the  $C_4$  and  $C_5$  normal fatty acids.

(23) *Molecular Volume*.—Pauly<sup>3</sup> tabulated the values of the molecular volumes of the chain acids  $C_1$  to  $C_8$  and claimed that a slight but definite alternation between the odd and even members of the series is observable

<sup>24</sup> *Chemical Abstracts*, 10, p. 2837.

<sup>25</sup> Tattersfield and Gimingham, *J. Soc. Chem. Ind.*, May 13 (1927).

<sup>26</sup> Siegler and Popenoe, *J. Econ. Entomol.*, 18, 292-99 (1925).

<sup>27</sup> Vorländer and Walter, *Z. physikal. Chem.*, 1925, 118, 1-30.

<sup>28</sup> Gurvich, *Koll. Z.*, 32, 80-91 (1923).

<sup>29</sup> Brown and Bury, *Trans. Chem. Soc.*, 123, 2430 (1923).

<sup>30</sup> Bartsche, *Koll. Chem. Beihefte*, 20, 7 (1925).

in the molecular volumes of the liquids *at the melting-points*. According to Garner and Ryder<sup>6</sup> this behaviour might be expected since the melting-points are alternating temperatures. These authors have determined the molecular volumes of a few acids, namely, octoic, nonoic, decoic, undecoic, and lauric at 50°. At this temperature the increments in molecular volume for each CH<sub>2</sub> group added to the chain are non-alternating and roughly constant, but the increment becomes a minimum in the neighbourhood of decoic acid (C<sub>10</sub>).

(24) *Vapour Pressure*.—The true "vapour pressure" of an expanded film is very small. Adam<sup>31</sup> gives the following values:—

Myristic acid	.	.	.	0.20	dynes per cm.
Palmitic acid	.	.	.	0.04	" " "
Ethyl stearate	.	.	.	0.025	" " "

It will be noted that there is a five-fold diminution in "vapour pressure" on passing from myristic (C<sub>14</sub>) to palmitic (C<sub>16</sub>) acid.

*Boiling-Points*.—The following table has been compiled from data given in International Critical Tables (Vol. I.):—

Normal Fatty Acid.	B. Pt. (° C.)	Δ.	Pressure mm.
C <sub>1</sub>	100.5		760
C <sub>2</sub>	118.1	+ 19.6	"
C <sub>3</sub>	141.1	+ 23.0	"
C <sub>4</sub>	163.5	+ 22.4	"
<u>C<sub>5</sub></u>	<u>187</u>	+ 23.5	"
C <sub>6</sub>	202	+ 15.0	"
C <sub>7</sub>	223.5	+ 21.5	"
C <sub>8</sub>	237.5	+ 14.0	"
C <sub>9</sub>	254	+ 16.5	"
C <sub>10</sub>	268.4	+ 14.4	"
C <sub>12</sub>	225		100
C <sub>13</sub>	236	+ 11.0	"
C <sub>14</sub>	250.5	+ 14.5	"
<u>C<sub>15</sub></u>	<u>257</u>	+ 6.5	"
C <sub>17</sub>	227	- 2 × 15.0	"
C <sub>19</sub>	299	+ 2 × 36	"

It will be noted that here the *differences* in boiling-point oscillate between the odd and even members, although in several cases the extent of the oscillation is small and may be due to experimental error. Superim-

<sup>31</sup> Adam, *Proc. Roy. Soc., A*, **110**, 423 (1926).

posed on these, however, are remarkable anomalies at  $C_6$  and  $C_{15}$ . In the latter instance the boiling-point itself exhibits an unmistakable maximum.

(25) *Complex Molecular Formation*.—Although Grün and Schacht<sup>32</sup> assume that in the interaction between glycerin-disulphuric acid and fatty acids complex molecular formation generally takes place, yet among the higher fatty acids used, it was only in the case of myristic acid ( $C_{14}$ ) that they met with success in isolating such a compound. The tendency of such complex formation decreases as the molecular weight increases.

(26) *Per Cent. Oxidation by  $H_2O_2$* .—Dakin<sup>33</sup> gives figures for the oxidation of 1/100 g. mol. of the ammonium salts of saturated fatty acids with 2/100 g. mol. of 3 per cent.  $H_2O_2$ . No claim to great accuracy is made but the results are comparative. The apparent per cent. oxidations (under the conditions considered) may be divided roughly into two groups (a) from  $C_1$  to  $C_5$ , (b) from  $C_6$  to  $C_{18}$ . In the latter group maxima occur in the oxidisability at the  $C_{10}$ ,  $C_{14}$ , and ( $C_8$ ) normal acids. Dakin's results seem to indicate that the  $C_6$ ,  $C_{10}$ , and  $C_{14}$  acids are abnormally reactive; this must be due to an enhanced residual affinity of these molecules. [In the case of myristic acid this receives further support from the experiments of Grün and Schacht.]<sup>32</sup>

(27) *Average Distance between Carbon Atoms*.—Donnan<sup>34</sup> has given the following values for the average distance between two carbon atoms in the fatty acids on the basis of Langmuir's theory, and N. K. Adam's results for the length of carbon chains. He found that the values (for  $C_{14}$  to  $C_{22}$ ) did not vary much from the value for the distance between the carbon atoms in the diamond.

Myristic acid	.	.	.	.	$1.6 \times 10^{-8}$ cm.
Pentadecylic acid	.	.	.	.	$1.6 \times 10^{-8}$ cm.
Stearic acid	.	.	.	.	$1.5 \times 10^{-8}$ cm.
Behenic acid	.	.	.	.	$1.5 \times 10^{-8}$ cm.

It is worth noting that the distance between the carbon atoms in the diamond ( $1.54 \times 10^{-8}$  cm.) lies between the values for the  $C_{15}$  and  $C_{16}$  chain acids.

(28) *X-ray Spacings*.—The X-ray examination of long-chain compounds is receiving considerable attention by various investigators, the outcome of which should prove interesting in relation to the form which the carbon chain assumes in space. Various authors have discussed the polymorphic forms of fatty acids. Clark<sup>35</sup> finds that the X-ray spacings for a paraffin-wax vary appreciably with the rate of cooling employed in preparing the sample for test. Nevertheless it is interesting to note that when the spacings  $d_1$   $d_2$   $d_3$  for the even-membered normal fatty acids ( $C_{12}$  to  $C_{22}$ ) obtained by Müller<sup>36</sup> are plotted against the number of carbon atoms in the molecule, there is a fairly well-defined maximum for each spacing at  $C_{14}$ . The variations in the side spacings  $d_2$  and  $d_3$  are perhaps the more striking.

Prins and Coster<sup>37</sup> have investigated higher order X-ray reflections from fatty acids. In the case of palmitic acid, for example, they find that the odd and even orders of reflection are roughly equally intense in the neighbourhood of the 9th order, whereas at the 16th (about as intense as the 5th) the even orders have much greater intensity. The authors consider that the scattering substance is not uniformly distributed along the chain but contains a periodicity due to the successive  $CH_2$  groups.

<sup>32</sup> Grün and Schacht, *Ber.*, 40, 1778.

<sup>33</sup> Dakin, *J. Biol. Chem.*, 1908, 229.

<sup>34</sup> Donnan, [Address to Section B., Brit. Assocn., 1923].

<sup>35</sup> Clark, *Nature*, 120, July. 2 (1927)

<sup>36</sup> Müller, *Trans. Chem. Soc.*, 2043 (1923).

<sup>37</sup> Prins and Coster, *Nature*, 118, 83-84 (1926).

### Sodium and Potassium Salts of Fatty Acids.

(29) *Capillary Activity*.—Donnan and Potts<sup>38</sup> have shown that the interfacial surface tension of a hydrocarbon-water surface is lowered by the sodium salts of the fatty acids. This lowering diminished up to sodium myristate ( $C_{14}$ ).

Lascaray<sup>39</sup> has measured the surface tension of aqueous solutions of pure sodium salts of the fatty acids at room temperature, using Traube's stalagmometer. Lascaray plots the surface tension against molecular weight and gives 7 iso-molar curves. The most striking feature of all these curves is a pronounced minimum surface tension at  $C_{14}$  (sodium myristate). [The  $C_{15}$  soap was not included in these experiments but  $C_{16}$ ,  $C_{18}$ , and  $C_{26}$  were.] When the surface tension is plotted against *molecular concentration* not only is the distance between the curves for  $C_4$  and  $C_6$  abnormally great, but whilst the  $C_4$  curve is *convex* to the concentration axis the  $C_6$  curve is *concave*. Between  $C_6$  and  $C_{14}$  "breaks" occur in all the curves investigated, but at  $C_{14}$  the "break" again disappears. From the general form of the curves  $C_6$ ,  $C_8$ ,  $C_{12}$  the possibility of another change in the neighbourhood of  $C_{10}$  is not excluded. Of the whole series of salts investigated sodium myristate ( $C_{14}$ ) has undoubtedly the highest capillary activity. There appears to be a zone of maximum colloidity in the region of  $C_{14}$ . Colloidal properties may begin at  $C_6$ . It is at  $C_{14}$  (or  $C_{15}$ ) that there is some fundamental change in the residual affinity of the molecule; the same remark applies but with less emphasis to the change at  $C_6$  (and possibly at  $C_{10}$ ).

(30) *Washing Power, Density, and Conductivity*.—Bunbury and Martin<sup>40</sup> find that "the appearance, washing power, density, and conductivity curve of potassium hexoate ( $C_6$ ) distinctly mark the beginning of that deviation from the behaviour of the acetate, which rapidly and regularly increases through the other members of the homologous series until it attains the typical character of the higher soaps." The decoate ( $C_{10}$ ) is the first to raise a typical lather. The authors also find that "potassium myristate and laurate are ideal soaps (for washing the hands) and the palmitate is almost as good but the stearate is much less so." Sodium myristate ( $C_{14}$ ) is good but sodium palmitate ( $C_{16}$ ) and stearate ( $C_{18}$ ) are quite useless.

### Other Homologous Series.

(31) *Molecular Moment*.—The following data refer to unsaturated hydrocarbons  $C_nH_{2n}$ . Smyth<sup>41</sup> has calculated the molecular moment for a number of typical organic substances by the use of the theory of Gans. The calculation makes use of the dielectric constant, the index of refraction, the density, and the molecular diameter and weight of the substance in question.

Amylene	.	.	.	.	.	.	.	0.49
Hexylene	.	.	.	.	.	.	.	0.28
Octylene	.	.	.	.	.	.	.	0.50
Decylene	.	.	.	.	.	.	.	0.55

There are apparent maxima at the fifth and tenth carbons in these unsaturated hydrocarbons.

(32) *Dielectric Constants*.—Richards and Shipley<sup>42</sup> give the following values:—

<sup>38</sup> Donnan and Potts, *Koll. Z.*, iv, 208 (1910).

<sup>39</sup> Lascaray, *Koll. Z.*, 34, 73 (1924).

<sup>40</sup> Bunbury and Martin, *Trans. Chm. Soc.*, 105, 435 (1914).

<sup>41</sup> Smyth, *J. Amer. Chem. Soc.*, 46, 2151 (1924).

<sup>42</sup> Richards and Shipley, *ibid.* (1919), p. 2011.

	D.C. at 20°.	
<i>n</i> -hexane . . . . .	1.876	Hexane (C <sub>6</sub> ) and Decane (C <sub>10</sub> ) have the lowest dielectric constants of these five normal saturated hydrocarbons.
<i>n</i> -heptane . . . . .	1.973	
<i>n</i> -octane . . . . .	1.962	
<i>n</i> -nonane . . . . .	1.967	
<i>n</i> -decane . . . . .	1.956	

The foregoing evidence is not intended to be exhaustive; there are signs, for example, of a similar periodicity in the refractive indices of the normal fatty acids, but all the data required for rendering a strict comparison possible do not appear to be available.

## THE SUMMARISED DATA.

Property.	Irregularity. Position of Carbon Atom in Chain.			Homologous Series.
Molecular rotatory power *	5	10	15	Ethyl-R-Carbinols.
Static friction . . . . .	4 and 5	†	15	" "
Cohesion of thin film . . . . .	—	—	15	" "
Density (D <sub>4</sub> <sup>20</sup> ) of liquid . . . . .	—	10 (?)	15	" "
Heat of crysn. (terminal groups)	5	10	15	Normal fatty acids.
Monomolecular films (packing density) . . . . .	5 or 6	10	15	" "
Electrical properties . . . . .	5 (?)	—	14	" "
Viscosity . . . . .	5	9	14 (or 15 ?)	" "
Surface pressure . . . . .	—	—	14 (or 15)	" "
Dissociation constant . . . . .	5	—	—	" "
Distance between C-atoms (Langmuir, Adam) . . . . .	—	—	15	" "
Smell strength . . . . .	5	—	—	" "
Magnetic rotation . . . . .	5	—	—	" "
Mol. vol. at 50° . . . . .	—	10	—	" "
Complex molecular formation . . . . .	—	—	14	" "
Foam-stability . . . . .	5	10 (?)	—	" "
Temperature surface solution . . . . .	—	—	14 or 15	" "
Toxicity . . . . .	5 or 6	11 (?)	14	" "
Heat of wetting . . . . .	5	—	—	" "
Heat of neutralisation . . . . .	5	—	—	" "
Esterification constants . . . . .	5	10	14 or 15	" "
Heat of combustion . . . . .	†	†	14 or 15	" "
Oxidation by H <sub>2</sub> O <sub>2</sub> . . . . .	5	10	14 (or 15 ?)	" "
Nernst's "n." . . . .	4 or 5	—	—	" "
Ind. double refraction . . . . .	4 or 5	9 or 10	—	" "
X-ray spacings (Müller) . . . . .	5 (7)	10	14 or 15	" "
Boiling-point . . . . .	5 (7)	—	15	" "
Capillary activity . . . . .	5	10 (?)	14 (or 15 ?)	Sodium salts of fatty acids.
Washing power, density, and conductivity . . . . .	6 (or 5 ?)	9	14 (or 15 ?)	Potassium salts.
Molecular moment . . . . .	5	—	—	Unsaturated hydrocarbons C <sub>n</sub> H <sub>2n</sub> .
Dielectric constants . . . . .	5 or 6	10	—	Methane series.
Foam-stability . . . . .	5	—	—	Normal primary alcohols.
				C <sub>n</sub> H <sub>2n</sub> + 1 . OH.

\* The most pronounced maxima in molecular rotatory power occurred at the 5th, 10th, and 15th C-atoms of the "growing-chain" R.

A dash (—) denotes lack of data.

† Denotes no irregularity observed.

Summarising, the evidence presented above shows that certain fundamental changes occur at (or in the immediate neighbourhood of) the 5th, 10th, and 15th carbon atoms of the chain.

### Summary and Conclusions.

From a consideration of a large number of properties such as static friction, adhesion, cohesion, surface tension, surface pressure and electrical properties of monomolecular films on water, viscosity dissociation constants, optical activity, magnetic rotation, toxicity, etc., cumulative evidence is adduced indicating that a well-defined irregularity or turning point exists in the properties of certain long chain compounds. This irregularity usually first becomes evident at the fifteenth carbon atom in the chain, although departure from the "normal" curve may actually begin at the fourteenth carbon atom. In many cases similar but less pronounced irregularities are found at the fifth and tenth carbon atoms. These remarks seem to apply to certain optically active carbinols as well as normal fatty acids and their salts. The data presented afford evidence in favour of the stereochemical view concerning the arrangement of carbon atoms in the form of a spiral or helix. It should be noted that although anomalies in molecular rotatory power have been detected at the 5th, 10th, and 15th carbon atoms in the optically active carbinols  $C_2H_5 \cdot CHOH \cdot C_nH_{2n+1}$ , yet these sudden increments in rotatory power were most marked at the 5th, 10th, and 15th carbon atoms of the "growing-chain."

The explanation advanced to account for these anomalous properties in homologous series is that the disposition of the carbon atoms in space is such as may cause a periodicity in those properties of the molecule which are ultimately dependent upon residual affinity. It thus appears that abnormalities in the electric moment (either inherent or induced) of similarly constituted compounds can be detected at (or in the immediate neighbourhood of) the 5th, 10th, and 15th carbon atoms in the chain.

From the foregoing considerations it would seem that polarity is a factor to be taken into account in connection with molecular rotatory power. This view is supported by the experiments of Rule and Mitchell,<sup>48</sup> who have shown that the influence of substituents on rotatory power is in approximate agreement with their polar character.

The evidence presented does not agree with the commonly accepted models of the carbon chain as deduced by X-ray analysis. If, however, we assume the correctness of these models for the solid state, then the gap may perhaps be bridged by ascribing to certain carbon atoms, together with the corresponding C-C linkages, the property of free rotation for long chain compounds in *solution*, in the *molten* or *other special state*; this would then permit the existence of an open-pentagonal type of structure and would not involve the complete rejection of the stereochemical ideas originated by van't Hoff and Baeyer. On this hypothesis, one might expect the increments in molecular volume for each  $CH_2$  group added to the chain to become non-alternating with respect to the odd and even members of a series at temperatures above the melting-point. Such evidence as is available tends to confirm this conclusion. It is hoped that publication of this paper may stimulate research into the question of periodic irregularities in the properties of members of homologous series.

<sup>48</sup> Rule and Mitchell, *Trans. Chem. Soc.* (1925), 127, 2188.

# THE ELECTROLYTIC OXIDATION OF PARA-TOLUIC ACID IN ALKALINE SOLUTION.

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As is known, the electrolytic oxidation of organic compounds has received but little practical application in comparison with cathodic reduction, the reasons being the relative sluggishness with which the anodic oxygen reacts with the depolariser and the fact that the reversible potentials for the onset of the oxidation and for the evolution of gaseous oxygen generally lie near to one another. The usual result is that much free oxygen is evolved at low current densities and the current efficiency for the oxidation in question is low, whilst, at higher current densities, owing to the fact that it is oxygen evolution, with its considerable overvoltage, which essentially determines the potential, the organic depolariser is oxidised more completely than is desired, and, in fact, may be burned up to carbon dioxide and water. Chiefly owing to the work of Grube and of his collaborators, it is known that, in somewhat similar cases in inorganic electrochemistry, the superposition of an alternating current on the direct current allows of considerable yields of the desired product being obtained, the immediate cause being the depression of the mean anodic potential below the figure required for oxygen evolution at the particular direct current density employed. Thus, both iron and lead, normally passive in alkaline solution, can be made to dissolve as ferrate<sup>1</sup> and plumbate<sup>2</sup> respectively by this means. In the field of organic electrochemistry, Reitlinger<sup>3</sup> was able, by the same device, to increase the current efficiency of electro-oxidation of ethyl alcohol to acetaldehyde in dilute sulphuric acid solution at platinum anodes, more particularly at high current densities, under which conditions Dony-Hénault<sup>4</sup> had shown further oxidation to acetic acid normally to occur.

The work described below was an attempt to apply the same method to the case of the oxidation of *p*-toluic acid in alkaline solution to terephthalic acid. Labhardt and Zschoche,<sup>5</sup> who had worked earlier on this reaction, had found platinum to be the best anodic material, and had shown the only products of oxidation to be terephthalic acid, carbon dioxide, and a small quantity of carbon monoxide. At low current densities much oxygen escaped unabsorbed, but the remainder gave terephthalic acid. At high current densities, whilst the absorption of oxygen increased, the actual yield of terephthalic acid fell off, owing to the formation of carbon dioxide. There appeared therefore the possibility that the superposition of a suitable alternating current might have the same effect as in the anodic solution of iron and the oxidation of ethyl alcohol. It may be stated at the outset that this anticipation was not realised—in whatever way the conditions were modified, there was in no single case an increase in the terephthalic acid yield.

<sup>1</sup> *Z. Elektrochem.*, **26**, 153 (1920).

<sup>2</sup> *Ibid.*, **28**, 275 (1922).

<sup>3</sup> *Ibid.*, **20**, 261 (1914).

<sup>4</sup> *Ibid.*, **6**, 533 (1900).

<sup>5</sup> *Ibid.*, **8**, 93 (1902).

### Apparatus and Procedure.

A 500 c.c. glass cylinder was closed by a large well-fitting rubber stopper, which carried a porous cell, a mercury-sealed glass stirrer, the glass tube into which was sealed the platinum anode, glass rod supports for the lower edge of the latter, a thermometer, a U-tube of wide bore through which cold water was circulated in order to keep down the temperature to about  $18^{\circ}$  during the electrolysis, and a delivery tube for taking off the anode gases. The porous pot contained the catholyte (a solution of caustic potash) and was open to the air. The cathode was a spiral of copper wire. The anode consisted, in some experiments, of a sheet of platinum foil, bent into the form of a cylinder and disposed concentrically around the porous pot. In order to obtain a well-defined current density, the outer surface of the anode, remote from the porous pot, was covered with a mixture of vaseline and paraffin wax, which preliminary trials had shown to be suitable for the purpose. It tended neither to be washed nor to be flaked off. The active area of the treated anode was  $81.4 \text{ cm}^2$ . In other experiments a flat platinum plate was used. The volume of the anolyte—a solution of *p*-toluic acid in excess of caustic potash—was normally 300 c.c.

The source of direct current was a small motor generator, manufactured by the General Electric Company, capable of a maximum output of 20 amperes at 30 volts. Alternating current of frequency 50 was furnished by a small 16-pole alternator (General Electric Company) and of frequency 500 by a machine made by Crocker and Wheeler. These alternators have been previously described in communications made from this laboratory.<sup>6</sup> When using compound currents,<sup>7</sup> the two generators were placed in parallel, the hot wire and moving coil ammeters suitably disposed, and the current leaks from one circuit into another determined by special measurements and allowed for. The currents used were hand-regulated to definite values throughout a run by means of sliding resistances. No difficulty was experienced in this.

In order to determine the percentage of anodic oxygen absorbed during the electrolysis, a second cell (II), containing as anolyte a solution of caustic potash free from *p*-toluic acid, was connected in series with the first (I), and the gases evolved from the two cells during electrolysis for a certain time interval measured, and, in the case of cell I, analysed. They consisted of oxygen and (from cell I) small amounts of carbon monoxide. No hydrogen was found, even when using high A.C. : D.C. ratios at a frequency of 50. Oxygen was determined by alkaline pyrogallol solution, and carbon monoxide by ammoniacal cuprous chloride.

Let  $a_1$  c.c. be the volume of  $\text{O}_2$  from cell I  
 $a_2$  c.c. be the volume of CO from cell I  
 $b$  c.c. be the volume of  $\text{O}_2$  from cell II.

Then

- (i) Volume of CO formed per volume of  $\text{O}_2$  originally discharged is  $\frac{a_2}{b}$ .
- (ii) Volume of  $\text{O}_2$  absorbed in cell I per volume of  $\text{O}_2$  originally discharged is  $\frac{b - a_1}{b}$ .
- (iii) Volume of CO formed per volume of  $\text{O}_2$  absorbed in cell I is  $\frac{a_2}{b - a_1}$ .

<sup>6</sup> *E.g. Trans. Far. Soc.*, 21, 1 (1925).

<sup>7</sup> Currents compounded of an alternating superposed on a direct current.

**Estimation of Terephthalic Acid.**—The fact was utilised that *p*-toluic acid is far more soluble than terephthalic acid in ordinary solvents. The method used by Labhardt and Zschoche was precipitation of the mixed acids after electrolysis by addition of a mineral acid, followed by extraction of the mixture with hot water. We were unable to obtain a satisfactory separation by this means and, after a number of trials, went over to the use of ether extraction at room temperature. The precipitate of the mixed acids was dried at 70° in an air oven, extracted in a beaker with 250 c.c. of ether, the clear solution decanted off through a weighed Gooch crucible, the residue extracted a second time with 100 c.c. of ether, the whole filtered through the Gooch crucible and the beaker finally washed out with water. The crucible containing the terephthalic acid was then dried at 70° to free it from water, washed with 75 c.c. of ether, re-dried and re-weighed. The method was tested with known mixtures of acids after dissolving them in caustic potash in proportions and under conditions corresponding to those of electrolysis.

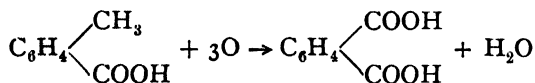
(i) *Taken*—0.6653 gram terephthalic acid and 9 grams *p*-toluic acid.

*Found*—0.6450 gram terephthalic acid.

(ii) *Taken*—0.7004 gram terephthalic acid and 9 grams *p*-toluic acid.

*Found*—0.6929 gram terephthalic acid.

As the equation involved is—



the formation of one mol. (166 grams) of terephthalic acid requires six gram-equivalents of oxygen. Hence, if  $n$  is the number of equivalents of oxygen discharged (calculated from the current used and duration of the electrolysis) and  $w$  the weight of terephthalic acid found, the current efficiency of its formation is—

$$100 \times \frac{6w}{166n} \text{ per cent.}$$

### Experiments with Direct Current.

**Effect of Concentration of Free Alkali.**—Preliminary experiments carried out over short periods of electrolysis, using 10 grams/300 c.c. of *p*-toluic acid and 4 amps./dm.<sup>2</sup> showed that the percentage of absorbed oxygen decreased as the concentration of free alkali was raised. At the same time, however, the electrolyte was observed to become reddish-brown in colour when the free alkali concentration was low. This change in colour was very rapid with a free alkali concentration of 0.5*N*, but was not noticeable during a short run with 2*N* or more concentrated alkaline solutions. For this reason, electrolytes 2*N* with respect to free alkali were used during the rest of the work. It may be mentioned that, during subsequent long-continued electrolyses, a slight darkening of the solution was frequently observed. On the other hand, the percentage of absorbed oxygen was found, under these conditions, to be considerably higher (57 to 61 per cent.—see Table I.) than was the case during the preliminary short runs referred to above (about 20 per cent.). This was presumably due to the anode potential not having reached its steady value during the short time of electrolysis. Similar, though smaller, effects, were observed later during experiments carried out with other current densities.

*Effect of Concentration of Acid (Salt).*—Keeping current density and free alkali concentration constant, the concentration of the acid was increased from 10 to 20 grams per 300 c.c. While this had the effect of increasing the proportion of absorbed oxygen, the terephthalic acid current efficiency remained at about the same figure—indeed, if anything, tended to fall. Clearly then, the increased concentration of depolariser was simply favouring those anode processes which were resulting in the complete break-down of the acid. The concentration of 10 grams/300 c.c. was therefore retained in subsequent work.

*Effect of Current Density on Oxygen Absorption.*—Keeping the other conditions constant, the current density was varied in a series of steps

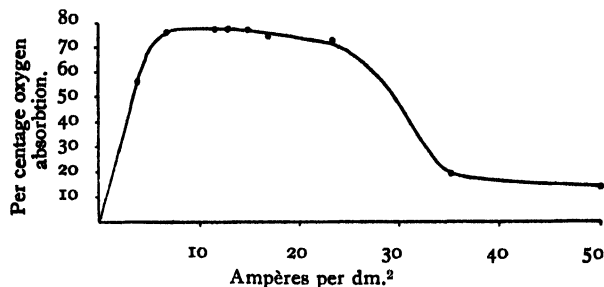


FIG. 1.

between the limits of 4 and 50 amps./dm.². The results are plotted in Fig. 1.

The chief features of the curve are (a) the sharp rise in absorption as current density is initially increased, (b) the current density

range from about 6 to 25 amps./dm.² over which the absorption exceeds 70 per cent. and is only slightly dependent on current density, (c) the rapid fall in oxygen absorption beyond about 30 amps./dm.².

*Effect of Current Density on Proportions of Products.*—To test this relation, current densities of 4 and 20 amps./dm.² were selected, and a series of electrolyses carried out over periods of 3 to 6 hours. The results are contained in Tables I. and II.

TABLE I.

OXYGEN ABSORPTION AND TEREPHTHALIC ACID CURRENT EFFICIENCY.

Current Density.	Percentage Oxygen Absorption.	Current Efficiency.	Percentage of Absorbed Oxygen Giving Terephthalic Acid.
4 amps./d.m.²	57.6	17.4	30.2
"	57.6	18.5	32.1
"	60.7	11.5	18.9
"	59.9	17.3	28.8
20 amps./d.m.²	78.4	8.0	10.2
"	60.8	5.6	9.2
"	66.35	7.4	11.2

The increase in current density and slight increase in total oxygen absorption are seen to be accompanied by (i) a marked fall in the fraction of the current used to produce terephthalic acid, (ii) a slight increase in the fraction used to produce carbon monoxide. As this slight increase and the corresponding increase in oxygen absorption run practically parallel to one another, the result is that the fraction of *absorbed* oxygen producing carbon monoxide is practically unaffected by current density. Just as with the increase in *p*-toluic acid concentration, the chief effect of raising the current density is

TABLE II.  
CARBON MONOXIDE PRODUCTION.

Current Density.	Percentage of CO in Anode Gases.	Volume of CO formed Per Volume of Oxygen Originally Discharged.	Volume of CO Per Volume of Absorbed Oxygen.
4 amps./d.m. <sup>2</sup>	3.9	0.017	0.029
"	3.5	0.015	0.026
20 amps./d.m. <sup>2</sup>	10.4	0.022	0.027
"	11.0	0.023	0.028

to increase the fraction of current employed in the complete break-down of the acid.

*Effect of Current Density on Anode Potential.*—It was natural to look for an explanation of the nature of Fig. 1 in the effect on the anode potential caused by increased current density, and the necessary measurements were therefore undertaken, using a Luggin capillary, an ordinary meter bridge, a Weston standard element, and a standard normal mercuric oxide electrode (in NaOH). The electrolytic bridge between the latter and the anolyte was of *N*. KOH. Measurements were first carried out with 2*N*. KOH free from *p*-toluic acid, the current density being altered in steps between the limits of 2 and 50 amps./dm.<sup>2</sup> Two sets of readings were made, one with rising, the other with falling, current densities. The usual time effects were noted, more marked with low than with high, and with rising than with falling, current densities. The curves in which were plotted the "final" figures (altering very slowly only) were not quite coincident, but cut at about 11.5 amps./dm.<sup>2</sup> and  $\pi_H = +1.87$  volts. A few typical readings are contained in Table III.

TABLE III.

Current Density.	Anode Potential.	
	Rising C.D.	Falling C.D.
5 amps./dm. <sup>2</sup>	+ 1.793 volts	+ 1.812 volts
10 "	1.859 "	1.863 "
20 "	1.915 "	1.900 "
30 "	1.940 "	1.920 "

With the solution containing *p*-toluic acid (10 grams/300 c.c., neutralised, and then made alkaline to the extent of 2*N* with KOH), the results were of interest. Four series of measurements were carried out. One of these appeared normal. The time effect was small, and the "final" figures, when plotted, lay on a more or less smooth curve. The results are in Table IV., the measurements being put in the order in which they were carried out, and plotted in Fig. 2, together with the average values obtained for pure KOH in absence of *p*-toluic acid.

The addition of the potassium *p*-toluate to the 2*N*. KOH is seen to have the effect of increasing the anode potential over the whole range of current density worked at.

In the other three experiments the curves, whilst following roughly the same course up to about 20 amps./dm.<sup>2</sup>, showed, at or about this current

TABLE IV.

Current Density.	Anode Potential.
50 amps./dm. <sup>2</sup>	+ 2.108 volts
34.9 "	2.037 "
20 "	1.958 "
4 "	1.878 "
2 "	1.838 "
20 "	1.958 "
34.9 "	2.057 "
50 "	2.098 "

TABLE V.

Current Density.	Anode Potential.
0.6 amps./dm. <sup>2</sup>	+ 1.670 volts
2 "	1.832 "
4 "	1.886 "
20 "	1.989 "
34.9 "	2.203 "
50 "	2.249 "
22.3 "	2.137 "
20 "	2.127 "
11.63 "	1.938 "
20 "	1.978 "
34.9 "	2.182 "
50 "	2.232 "

density, a marked break, the anode potential suddenly rising by over 0.1 volt, and then pursuing anew a "normal" course. When working in the

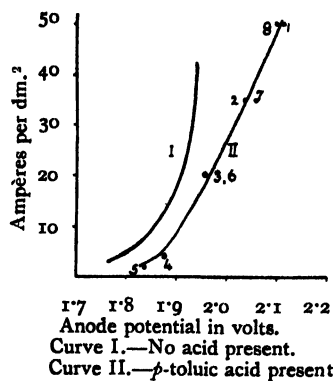


FIG. 2.

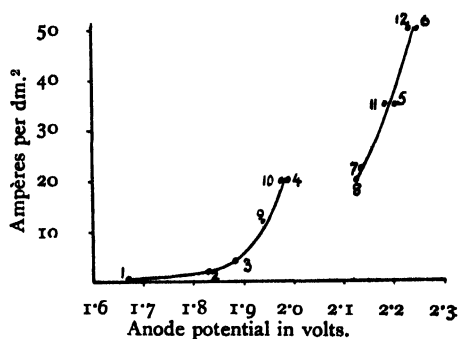


FIG. 3.

reverse direction, *i.e.* with falling current densities, the same break was noted at about the same current density. The figures for the most complete of these experiments are contained in Table V. and plotted in Fig. 3.

### Discussion.

In our experiments, it was invariably noticed that, during electrolysis, a film of precipitated acid was formed on the electrode which, although continually torn off and dispersed by the evolved oxygen, just as continually renewed itself. This film formation is doubtless caused by a local decrease in alkalinity in the electrode layer due to OH<sup>-</sup> ion discharge, resulting in the precipitation of *p*-toluic, or perhaps terephthalic, acid. Whether owing to a local increase in H<sup>+</sup> ion concentration or to a decrease in the active area of the anode, the fact that the anode potential is higher in presence of the depolariser than it is in the pure alkaline solution is sufficiently explained. *p*-Toluic acid is a slowly acting acceptor of oxygen, and any depolarising action it exerts on the anode potential under these conditions is more than counteracted by the effects just mentioned. The sudden changes noted at about 20 amps./dm.<sup>2</sup> can readily be explained by the assumption that the film formation becomes more intense above this current density than can be dealt with by the disintegrating action of the evolved oxygen, and thereby

seriously interferes with the active area of the anode. This *continuous* film effect will clearly, from its nature, set in suddenly, and the resulting high current density and very localised oxygen discharge, with which the processes of diffusion and migration which bring the depolariser to the anode can no longer keep pace, will cause the jump in anodic potential (Fig. 3) and the sudden fall in utilisation of discharged oxygen (Fig. 1) which are observed. The differences between Figs. 2 and 3 are probably due to an unremarked difference in efficiency of stirring or such similar cause, whilst the large differences between the percentage oxygen absorptions (61 and 78 per cent.) at 20 amps./dm.<sup>2</sup> (Table I.) can readily be understood in the light of Fig. 3.

### Experiments with Compound Currents.

These were done at the two standard direct current densities (4 and 20 amps./dm.<sup>2</sup>) employed above, and with frequencies of 50 and of 500, the A.C. : D.C. ratio being varied over a considerable range.

*Low Frequency: Low Current Density.*—In these experiments the A.C. : D.C. ratio was varied between 2 and 0.1. For low values of this ratio (up to 0.5), the percentage absorption of direct current oxygen was hardly affected by the alternating current component. The wave form of such compound currents is that of a periodic direct current, the amplitude of the periods increasing with increase in the A.C. : D.C. ratio, and no actual current reversal takes place. When, however, the value of the ratio exceeds 0.7 (*i.e.*  $1 : \sqrt{2}$ ), this reversal sets in, *i.e.* the current now contains a *cathodic* component. Corresponding to the reaching of this critical value, a very marked drop in oxygen absorption was noted at an A.C. : D.C. figure of 0.75. From being about 60 per cent., it sank to 20.8 per cent. (two experiments) whilst a further increase to a ratio of 2 led to a drop in oxygen absorption down to 2.6 per cent. (mean of three experiments). This type of result is well known in work of this kind—the diminution in the oxygen content of the electrode brought about by H<sup>+</sup> ion discharge during the cathodic pulse results in the potential being lowered to a figure at which oxidation of the depolariser becomes excessively slow or even impossible.

The terephthalic acid yields, on the other hand, commence to fall at lower A.C. : D.C. ratios, before any effect is visible on the total oxygen absorption. These points are shown in Table VI., which gives average figures for a number of experiments, and which should be compared with Table I.

TABLE VI.  
LOW FREQUENCY: LOW C.D.

A.C. : D.C. Ratio.	Percentage Oxygen Absorption.	Terephthalic Acid Current Efficiency.	Percentage of Absorbed Oxygen Giving Terephthalic Acid.
1 : 10	> 45 <sup>a</sup>	9.6	> 21
1 : 4	66	9.8	15
1 : 2	61	5.2	8.5
3 : 4	21	0	0
2 : 1	2.6	0	0

On the other hand, the proportion of absorbed oxygen giving carbon monoxide increases slightly, the figures for those experiments in which appreci-

<sup>a</sup> Not corrected for CO content of anode gases.

able oxygen absorption took place always exceeding 3 per cent. and averaging 3.5 per cent. (compare Table II.). It may be added that, with the A.C. : D.C. ratio of 2 : 1, the platinum anode became covered with a plainly visible yellow film<sup>9</sup> and liberated iodine on being dipped into an acidified KI solution. With smaller ratios, no visible film was formed, but the anode still liberated iodine from an acidified KI solution as before, though in smaller amounts.

*Low Frequency : High Current Density.*—The same range of A.C. : D.C. ratios was covered, attention being chiefly paid to the question of terephthalic acid production. The average figures are given in Table VII.

TABLE VII.  
LOW FREQUENCY : HIGH C.D.

A.C. : D.C. Ratio.	Terephthalic Acid Current Efficiency.
1 : 10	5.9
1 : 4	6.3
1 : 2	6.6
1 : $\sqrt{2}$	1.0
1 : 1	0
2 : 1	0

Comparison with Tables I. and VI. shows the same type of effect as with the lower current density, although considerably less pronounced. The proportion of absorbed oxygen giving carbon monoxide was tested in two cases, and was found to be practically the same as with direct current only (Table II.).

*High Frequency : Low Current Density.*—The A.C. : D.C. ratio used were 2 : 1, 1 : 1, and 1 : 2. The results are in Table VIII., and it will be seen, when compared with Table VI., that the effect of increasing the frequency is very marked. Even with the ratio 2 : 1, the current efficiency has not fallen to zero, whilst with the 1 : 1 value (cathodic pulse present), it is practically the same as that given by an ordinary direct current (Table I.).

TABLE VIII.  
HIGH FREQUENCY : LOW C.D.

A.C. : D.C. Ratio.	Current Efficiency.
1 : 2	14.5
1 : 1	16.8
2 : 1	3.0

TABLE IX.  
HIGH FREQUENCY : HIGH C.D.

A.C. : D.C. Ratio.	Current Efficiency.
1 : 2	2.8 (?)
1 : $\sqrt{2}$	3.8
1 : 1	1.4
2 : 1	1.0

*High Frequency : High Current Density.*—See Table IX. When compared with Table VII., the effect of frequency is again very marked in the last three cases.

*Anode Potential Measurements.*—These were carried out in the usual way, using a platinum plate electrode, and measuring the direct current by a moving coil milliammeter and the alternating current by a Duddell thermogalvanometer. As not the absolute values, but their relations to the figures given by direct current alone under the same conditions, were of chief

<sup>9</sup> Cf. Grube and Dulk, *Elektrochem.*, 24, 237 (1918).

interest to us, measurements were taken alternately with direct and with compound currents, the differences being noted. No attempt was made to evaluate liquid potential differences. The time effect in these experiments was small, the final values, within the limit of experimental error, being usually attained in a few minutes. The readings in general, however, were not as steady or as reproducible as when using direct current alone. Omitting one set of measurements obtained with  $n = 50$  and the direct current density of 20 amps./dm.<sup>2</sup>, which seemed undoubtedly, for some reason, abnormal, the results are summarised in Table X, which gives the lowerings in anode potential expressed in millivolts.

TABLE X.

A.C. : D.C. Ratio.	Frequency 50.		Frequency 500.	
	Direct Current Density 4 Amps./dm. <sup>2</sup> .	Direct Current Density 20 Amps./dm. <sup>2</sup> .	Direct Current Density 4 Amps./dm. <sup>2</sup> .	Direct Current Density 20 Amps./dm. <sup>2</sup> .
1 : 10	—	10	—	—
1 : 4	—	15	10 ; 10	8 ; 7 ; 7
1 : 2	30	81 ; 100 ; 70	41 ; 43	36 ; 20 ; 31 ; 27
3 : 4	113	—	—	—
1 : 1	277	944 ; 411 ; 392	143 ; 143 ; 137	494 ; 448
2 : 1	709	985 ; 974 ; 974	641 ; 618 ; 632	1128 ; 1152
3 : 1	960	—	—	—

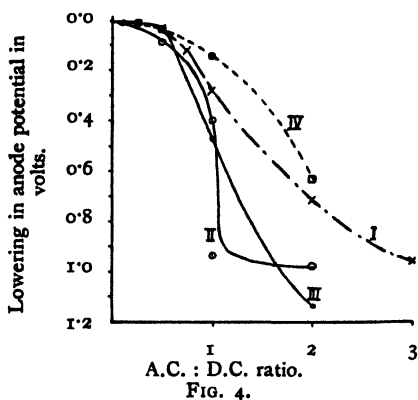
The following points emerge from a consideration of this Table:—

(i) Neglecting the small differences in the reverse sense shown in the experiments with  $n = 500$  and low A.C. : D.C. ratios, the lowering in anode potential is greater at higher than at lower current densities.

(ii) With two exceptions, of which one is undoubted (A.C. : D.C. ratio = 2, current density of 20 amps./dm.<sup>2</sup>), the lowering in anode potential is greater, the lower the frequency.

(iii) Whereas, in the other cases, duplicate readings agree with one another within experimental error, this is not so for the experiments at  $n = 50$ , A.C. : D.C. ratio = 1, and current density = 20 amps./dm.<sup>2</sup>. The marked discrepancy indicates a sudden change in direction at this A.C. : D.C. ratio figure of the curve connecting anode potential and A.C. : D.C. ratio. Bearing these facts in mind, the mean values of the data in Table X. (with the exception just mentioned, where *both* figures are included) are plotted in Fig. 4.

It will be seen that, as we interpret the experimental data, the curves for  $n = 50$  (I and II) drop sharply at A.C. : D.C. ratios in the region of 0.7-1 (*i.e.* at alternating current values at which the pulsating direct current changes over to an asymmetrical alternating current) and then flatten out again. The curve for  $n = 500$  and the higher current density (III) drops about as rapidly, but shows no very definite signs of bending over, whilst



the change of potential with the higher frequency current at the lower current density (curve IV) is more gradual. The fact that the potential lowering at the A.C. : D.C. ratio of 2 : 1 and with a direct current density of 20 amps./dm.<sup>2</sup> is greater with high than with low frequency current is a quite unexpected result.

### Discussion.

As mentioned already, in no single case, with high or low frequency, with high or low current density, was an improvement effected in the direct current yield of terephthalic acid by superposition of alternating currents. The explanation can only lie in the nature of the anodic processes involved. These are (i) evolution of unutilised oxygen, (ii) oxidation of *p*-toluic acid to terephthalic acid, (iii) complete oxidation of *p*-toluic acid with formation of CO and CO<sub>2</sub>. Processes (ii) and (iii) would appear to set in at potentials not far removed from one another, and, although the fact that a greater proportion of absorbed oxygen is utilised in forming terephthalic acid at low than at high current densities (Table I.) indicates that (ii) perhaps commences before (iii), yet its velocity is so small that, in practice, this possibility cannot be utilised, as process (i) completely dwarfs the others at really low anode potentials. It is this last circumstance which is really responsible for the lack of success of the use of a superposed alternating current in the present instance, a circumstance not present in the case of the oxidation of ethyl alcohol.

At first sight it may nevertheless appear surprising that, when the average anode potential is lowered by the superposition of an alternating current, the result is to favour (iii) as compared with (ii) (Table VI.). We are of opinion that the reason for this is only likely to be found by a closer study of the mechanism of these processes by means of oscillographic measurements, and we are not yet in a position to undertake the latter. In any case, it is, as matters stand, impossible to trace any connection between the different terephthalic acid yields and the average anodic potentials (Tables VI.-X. and Fig. 4).

### Summary.

(1) The electrolytic oxidation of alkaline solutions of *p*-toluic acid at a platinum anode has been studied at room temperature.

(2) The most favourable conditions found were: *electrolyte*—*N/4* potassium *p*-toluate (about)—*2N* potassium hydroxide; *current density*—4 amps./dm.<sup>2</sup> Under these conditions the average current efficiency is 16 per cent.

(3) A decrease in the free alkali concentration gives discoloured solutions, whilst the yield is lowered by an increase in either alkali or salt concentration, or by an increase or decrease in current density.

(4) The effect of superposing an alternating current is either negative (with small currents of frequency 500) or unfavourable (with currents of frequency 50 or with large currents of frequency 500).

(5) Anode potential measurements have been made throughout.

This work was carried out during the sessions 1924-26. We are indebted to the firm of Brunner, Mond & Company, Ltd., for a fund which enabled us to purchase the direct current generator used in the experiments.

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# HYDROLYSIS OF THE PEPTIDE (—CO—NH—) LINKAGE.

BY A. I. ESCOLME AND W. C. M. LEWIS.

*Received 24th August, 1927.*

The object of the present work was to determine in as quantitative a manner as possible the energy changes involved in the hydrolysis of the peptide (—CO—NH—) linkage, mainly because of the important part which this linkage plays in the chemistry of the protein molecule.

Two types of substance suggest themselves for examination, (1) a dipeptide, *e.g.*, glycyl glycine, (2) a substituted amino acid, *e.g.*, acetyl glycine.

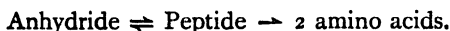
Examining the first type, Jaitschnikow<sup>1</sup> finds that both at 10° and 100° C. the hydrolysis of glycyl glycine proceeds for about one-third of its course in accordance with the equation for a reaction of the first order. The reason for the gradual decrease in the numerical value of the velocity constant is that a secondary, simultaneous reaction takes place causing the effective concentration of glycyl glycine to decrease owing to its partial conversion into its anhydride (diketopiperazine), the latter substance being non-estimable by the formol titre method employed by Jaitschnikow.<sup>2</sup>

Jaitschnikow also used Fischer's data on the hydrolysis of d-alanyl-d-alanine<sup>3</sup> and glycyl-d-alanine,<sup>4</sup> by means of hydrochloric acid to show that the reaction proceeds throughout its course in accordance with the equation for a unimolecular process. In these two cases, the hydrolysis was followed by means of a polarimeter since these dipeptides are optically active.

Levene, Simms, and Pfaltz<sup>5</sup> have examined the following dipeptides: Glycyl glycine, sarcosyl glycine, glycyl sarcosine and sarcosyl sarcosine. It was found that three reactions occurred simultaneously:—

- (a) The peptide was split irreversibly into amino acids (the true hydrolytic process).
- (b) The peptide formed a ring compound of the type of diketopiperazine.
- (c) The anhydride opened up forming peptide.

These reactions are formulated thus—



Referring to substances of the second type, *i.e.*, to substituted amino acids, the two most easily prepared, namely, acetyl glycine ( $\text{CH}_3\text{CO—NHCH}_2\text{COOH}$ ) and benzoyl glycine ( $\text{C}_6\text{H}_5\text{CO—NHCH}_2\text{COOH}$ ) are dealt with here. The advantage of the substituted amino acid over a dipeptide is that ring formation, analogous to the type of diketopiperazine, is impossible and consequently such bodies lend themselves to more precise investigation.

<sup>1</sup> *J. Russ. Physic. Chem. Soc.*, **52**, 147, 1920.

<sup>2</sup> The writers are indebted to Dr. F. W. Kay, Lecturer in Organic Chemistry of this University, for translating Jaitschnikow's original Russian paper.

<sup>3</sup> *Ber.*, **39**, 466, 1906.

<sup>4</sup> *J. Biol. Chem.*, **61**, 445, 1924.

<sup>5</sup> *Ber.*, **40**, 947, 1907.

### Hydrolysis of Acetyl Glycine by Hydrochloric Acid in Aqueous Solution.

The acetyl glycine was prepared essentially by the method of Curtius<sup>6</sup> the yield being 70 per cent. of the theoretical. As criterion of purity the melting-point was found to correspond with that found by Curtius (206° C.) and on fully hydrolysing a solution of the substance, the amount of glycine experimentally determined corresponded with that required by theory.

The unimolecular velocity constants summarised below refer to 60° and 70° C. The concentrations of hydrochloric acid employed were 0.25, 0.5 and 1.0 normal respectively. The degree of hydrolysis after a given time was obtained by estimating the quantity of amino acid (glycine) in the reaction mixture by means of the Van Slyke method.<sup>7</sup> Acetyl glycine is not very soluble in water and hence the volumes of nitrogen liberated are small. Because of this the standard Van Slyke deaminiser was used while the volume of nitrogen gas was measured in a micro-burette. The precautions recommended by Van Slyke were carefully followed.

It was found by experiment that the rate of hydrolysis could be conveniently followed at 60° C. and above, and further that the hydrolysis proceeded in each case to completion.

The velocity constants are given in reciprocal seconds, logarithms to the base *e* being employed. One set of results only is quoted in full (Table I.) to indicate the degree of constancy obtained. The mean values are summarised in Table II.

TABLE I.

*Initial Composition.*—5.7193 grams of acetyl glycine in one litre of 0.5 normal hydrochloric acid. *Temperature* 60° C.

Time. Hours. Minutes.		Vol. of Gas Evolved in C.cs. at N.T.P.	$k \times 10^6$ Secs. -1.	Time. Hours. Minutes.		Vol. of Gas Evolved in C.cs. at N.T.P.	$k \times 10^6$ Secs. -1
0	0	0.77	—	0	0	0.77	—
12	0	4.09	7.94	10	50	3.79	8.10
16	10	4.99	7.92	18	5	5.34	7.85
20	45	5.85	7.87	22	5	6.14	7.98
24	5	6.46	7.94	35	15	8.10	8.08
34	40	8.04	8.06	41	45	8.70	7.87
∞		12.20	—	∞		12.20	—
Average $k = 7.94$				Average $k = 7.97$			

$$\text{Mean } k = 7.96 \times 10^{-6}$$

TABLE II.

Concentration of Hydrochloric Acid.	$k \times 10^6$ 60° C.	$k \times 10^6$ 70° C.	E in Calories Per Mole.
0.25 N.	4.12	1.10	22,300
0.5 N.	7.96	2.11	22,100
1.0 N.	15.4	4.04	21,900

<sup>6</sup> *Ber.*, 17, 1865, 1884.

<sup>7</sup> *J. Biol. Chem.*, 9, 185, 1911.

The critical increment  $E$  of activation characteristic of the process is given in the final column of the above table. It is obtained from the usual equation—

$$\frac{d \log k}{dT} = \frac{E}{RT^2}.$$

The above value of 22,000 calories is a surprisingly small one considering the slowness of the reaction, for it will be observed that the hydrolysis of the peptide link only proceeds measurably at a relatively high temperature and with relatively high concentration of acid. The value of  $E$  is very nearly that characteristic of the inversion of sucrose, which proceeds much more easily. This point is dealt with later.

The hydrolysis is obviously catalysed by the acid, but it is evident at the same time that, from the data obtained, it would be impossible with any degree of confidence to distinguish between the volume concentration of the hydrogen ion (taking the acid as sensibly completely ionised) as the correct function and the activity of the hydrogen ion, since, over the range covered, the latter varies in approximately the same manner as the concentration values themselves.

The activity values were obtained by the *E.M.F.* method using a cell of the type:—

Hydrogen	:	Hydrochloric	:	Saturated	:	Normal
electrode	:	acid	:	potassium	:	calomel
			:	chloride	:	electrode

at 25° C.

It was recognised that the necessity of using an intermediate liquid introduced a certain amount of error in the activity values. For this reason the activity values are only expressed in two places. The absolute value of the normal calomel was taken to be 0.5648 volt. The equation  $\pi_H = 0.282 + 0.059 \log_{10} a_{H^+}$  was employed, where  $a_{H^+}$  is the activity of the hydrogen ion.

The following values were obtained—

Concentration of Hydrochloric Acid.	Mean <i>E.M.F.</i> of Cell in Volts. (Corrected for Barometric Pressure.)	$a_{H^+}$ .
0.25 <i>N.</i>	0.3242	0.20
0.5 <i>N.</i>	0.3072	0.39
1.0 <i>N.</i>	0.2872	0.84

The activity of the water vapour which may also be involved as one of the terms in the process falls approximately by 2 per cent. over the acid concentration range referred to.

To attempt to determine whether it is concentration of hydrogen ion or its activity which enters and whether the water vapour term enters at all or not, it is necessary to choose more suitable conditions than those represented by a simple aqueous solution. With this object, the necessary determinations have been carried out in solvents which consist of mixtures of water and a suitable organic liquid. The first case dealt with was that of water-glycerol mixtures.

*The Hydrolysis of Acetyl Glycine by 0.5 N. Hydrochloric Acid in Presence of Glycerol.*

The glycerol employed (B.D.H.) was redistilled in vacuo. In using the Van Slyke method already described, it was found necessary to shake for a much longer time when glycerol was present. Thus in presence of 50.4 per cent. glycerol, shaking for one hour was necessary for the complete evolution of amino nitrogen.

The mean velocity constants are given in the following table (Table III.).

TABLE III. CONCENTRATION OF HYDROCHLORIC ACID = 0.5 N.

Grams of Glycerol Per 100 C.cs. Solution.	$k \times 10^6$ 60° C.	$k \times 10^5$ 70° C.	E in Calories.
0	7.96	2.11	22,100
12.6	8.57	2.24	21,800
31.5	9.14	2.38	21,700
50.4	9.55	2.50	21,800

It will be seen that the addition of glycerol causes a gradual *increase* in the value of the observed velocity constants.

The addition of the glycerol is at the same time without influence on the magnitude of the apparent critical increment. This is significant in view of the fact that in the case of the decomposition of triethyl sulphonium bromide, which is regarded as a *truly* unimolecular process, alteration in the composition of the solvent has a measurable influence upon the magnitude of the critical increment, as shown by the work of R. F. Corran.

The activity of the hydrogen ion in 0.5 N hydrochloric acid in presence of various amounts of glycerol has been determined at 25° C., using the same type of cell as before. It was found that a much longer time was necessary to enable the cell to attain a steady value, the time increasing as the concentration of the glycerol increased.

Table IV. gives the results so obtained, the values quoted being corrected for the barometric pressure.

TABLE IV. 0.5 NORMAL HYDROCHLORIC ACID AT 25° C.

Grams of Glycerol Per 100 C.cs. of Solution.	Mean E.M.F. Volts.	$a_{H^+}$
0	0.3072	0.39
12.6	0.3045	0.43
31.5	0.3003	0.50
50.4	0.2961	0.595

Values for the activity of water in the above solutions have been obtained from the vapour pressure measurements (at 70° C.) of Perman and Price<sup>8</sup> and are given in Table V.

As regards the nature of the hydrolytic process, several possible mechanisms suggest themselves as feasible. The real difficulty in dealing with any one of them is that it is by no means certain whether one should adopt the "activity theory" of reaction velocity or whether recourse should

<sup>8</sup> *Trans Faraday Soc.*, 8, 74, 1912.

be had to the theory of Brönsted and Bjerrum. The difficulty in the latter is the determination of the activity coefficient of the intermediate complex. It will be observed also that up to this point nothing has been said about the activity of the acetyl glycine itself. Its actual volume concentration is in all cases low, not exceeding 0.055 molar in the case of water + glycerol as solvent. If one were to adopt molar fraction as a rough measure of activity one obtains values which alter greatly with glycerol content, to such an extent, indeed, as scarcely to be thought probable. It might have been thought that solubility determinations would have given at least an approximate measure of the quantity desired, but as will be pointed out later, the remarkable contrast in behaviour as regards solubility presented by acetyl glycine and benzoyl glycine respectively and the close similarity of these two substances in respect of chemical kinetics show that solubility measurements are of little use in this case. (See section on solubility relations.) It has been deemed best, therefore, not to attempt the elucidation of the complete mechanism but to see instead to what extent the reduction of the observed velocity constants to a standard hydrogen ion activity and to a standard water activity would lead to values more or less independent of variations in solvent. This step is at least necessary as a preliminary. For this reason the values of  $\frac{k}{a_{H^+}}$  and  $\frac{k}{a_{H^+} \times a_{H_2O}}$ , the "reduced" velocity constants, are both given in the following table. The values refer to 60° C.

TABLE V.

SOLVENT: WATER.

Concentration of Hydrochloric Acid.	$k \times 10^6$ .	$a_{H^+}$ .	$a_{H_2O}$ .	$\frac{k}{a_{H^+}}$ .	$\frac{k}{a_{H^+} \times a_{H_2O}}$ .
0.25 N.	4.12	0.20	0.98	20.6	21.0
0.5 N.	7.96	0.39	0.975	20.4	20.9
1.0 N.	15.4	0.84	0.96	18.3	19.1

SOLVENT: WATER + GLYCEROL. (0.5 N. HCl.)

Grams Glycerol Per 100 C.cs. of Solution.	$k \times 10^6$ .	$a_{H^+}$ .	$a_{H_2O}$ .	$\frac{k}{a_{H^+}}$ .	$\frac{k}{a_{H^+} \times a_{H_2O}}$ .
0	7.96	0.39	0.975	20.4	20.9
12.6	8.57	0.43	0.96	19.9	20.7
31.5	9.14	0.50	0.90	18.3	20.3
50.4	9.55	0.595	0.82	16.05	19.6

It will be observed that  $\frac{k}{a_{H^+} \times a_{H_2O}}$  is more constant than is  $\frac{k}{a_{H^+}}$ . At the same time the actual alteration of the observed velocity constant with glycerol is (rather remarkably) not large. Similar determinations were therefore carried out in another solvent, namely water + propyl alcohol.

*The Hydrolysis of Acetyl Glycine by 0.5 N. Hydrochloric Acid in Presence of Propyl Alcohol.*

The propyl alcohol (B.D.H.) was dried over freshly ignited quicklime and redistilled, the fraction passing over between 97° C. – 98° C. being collected and used. In the usual Van Slyke method, it was found necessary, as in the case of glycerol, to shake for a much longer time for the complete evolution of the nitrogen than is necessary in the absence of the propyl alcohol.

The unimolecular velocity constants are given in the following table:—

TABLE VI. CONCENTRATION OF HYDROCHLORIC ACID, 0.5 N.

Grams Propyl Alcohol Per 100 C.cs. Solution.	$k \times 10^6$ 60° C.	$k \times 10^6$ 70° C.	E in Calories.
0	7.96	2.11	22,100
8.08	10.51	2.83	22,500
20.2	9.79	2.57	21,900
32.3	8.46	2.23	21,900

It will be seen that the velocity constant increases rapidly on the addition of small concentrations of propyl alcohol and on further addition the observed velocity constant passes through a maximum and then falls steadily. At the same time there is no appreciable alteration in the critical increment.

The activity of hydrogen ion in 0.5 N. hydrochloric acid in presence of different amounts of propyl alcohol has been determined as before. A very long time was necessary before the cell attained a steady value. In the highest concentrations of propyl alcohol used, the time required was from 3 to 5 days and it was difficult to obtain concordant readings. The results are given in the following table:—

TABLE VII. CONCENTRATION OF HYDROCHLORIC ACID 0.5 N.

Grams Propyl Alcohol Per 100 C.cs. Solution.	E.M.F. Corrected for Barometric Pressure.	$a_{H^+}$
0	0.3072	0.39
8.08	0.3040 0.3042 0.3043	0.44
20.2	0.3062 0.3066 0.3066	0.40
32.3	0.3086 0.3084 0.3082	0.37

The fact that the  $a_{H^+}$  passes through a maximum at the same position as that at which the observed velocity constant likewise passes through a maximum is the most direct evidence we have yet obtained that in this reaction the activity of the hydrogen ion is the correct function to employ.

The activity of water was obtained from the vapour pressure data of Wrewsky<sup>9</sup> at 79.8° C., and the values are included in Table VIII.

<sup>9</sup> *Z. physikal Chem.*, 81, 1, 1913.

TABLE VIII. CONCENTRATION OF HYDROCHLORIC ACID 0.5 N.

Grams Propyl Alcohol Per 100 C.cs. of Solution.	$k \times 10^6$ .	$a_{H^+}$ .	$a_{H_2O}$ .	$\frac{k}{a_{H^+}}$ .	$\frac{k}{a_{H^+} \times a_{H_2O}}$ .
0	7.96	0.39	0.975	20.4	20.9
8.08	10.51	0.44	0.97	23.9	24.6
20.2	9.79	0.40	0.955	24.5	25.65
32.2	8.46	0.37	0.94	22.9	24.4

There is little to choose between either of the expressions for neither is capable of obliterating the maximum although it is reduced.

*The Effect of the Addition of Potassium Chloride on the Hydrolysis of Acetyl Glycine by 0.5 N. Hydrochloric Acid.*

Since potassium chloride is a strong electrolyte, the addition of this salt to a reaction mixture will, among other things, introduce electrical effects which are negligible when non-electrolytes, such as glycerol or propyl alcohol are used as water displacing agents. It is of interest, however, to see what effect is produced upon the velocity constant. The values are given in the following table:—

TABLE IX. CONCENTRATION OF HYDROCHLORIC ACID 0.5 N.

Grams KCl Per 100 C.cs. Solution.	$k \times 10^6$ 60° C.	$k \times 10^6$ 70° C.	E in Calories.
0	7.96	2.10	22,100
5	8.08	2.19	22,600
10	8.30	2.27	22,800
20	8.69	2.37	22,800

As in the case when glycerol was added to the reaction mixture a steady, very slow, rise in the observed velocity constant accompanies an increase in potassium chloride content. It is noteworthy that the addition of potassium chloride does not appreciably affect the critical increment.

The activity of hydrogen ion in 0.5 normal hydrochloric acid in presence of the above amount of potassium chloride has been determined as before at 25° C. The results are as follows:—

Grams KCl per 100 c.cs. solution :      0              5              10              20  
 $a_{H^+}$  . . . . .      0.386    0.435    0.544    0.738

The activity of water in the potassium chloride solutions has been obtained from the vapour pressure data at 70° C. of Perman and Price.<sup>8</sup> The values are given in Table X.

TABLE X. CONCENTRATION OF HYDROCHLORIC ACID 0.5 N.

Grams KCl Per 100 C.cs. Solution.	$k \times 10^6$ 60° C.	$a_{H^+}$ .	$a_{H_2O}$ .	$\frac{k}{a_{H^+}}$ .	$\frac{k}{a_{H^+} \times a_{H_2O}}$ .
0	7.96	0.39	0.975	20.4	20.9
5	8.08	0.435	0.965	18.6	19.3
10	8.30	0.54	0.94	15.4	16.4
20	8.69	0.74	0.89	11.7	13.1

Neither expression is even approximately constant. We have here evidence that in the presence of strong electrolyte the activity theory breaks down and must be replaced by one such as that of Brönsted and Bjerrum.

**The Hydrolysis of Benzoyl Glycine by Hydrochloric Acid in Aqueous Solution.**

Like acetyl glycine, benzoyl glycine or hippuric acid, on hydrolysis gives an acid (benzoic acid) and glycine. It was found to be distinctly more stable than the acetyl derivative and the velocity constants were consequently determined at 80° and 90° C. by a technique similar to that already described. The maximum concentration of benzoyl glycine employed did not exceed 0.058 mols. per litre. The relative values of the activity of hydrogen ion and of water were obtained as before.

The benzoyl glycine (B.D.H.) was recrystallised three times from hot water and dried in a vacuum dessicator. The melting-point was 187° C., the accepted value. The substance was found to be free from amino acid. After complete hydrolysis, the volume of nitrogen obtained corresponded with that required by theory. The following table contains the observed unimolecular velocity constants in aqueous solution with varying amounts of catalyst.

TABLE XI.

Concentration of Hydrochloric Acid.	$k \times 10^6$ 80° C.	$k \times 10^6$ 90° C.	E in Calories.
0.25 N.	1.009	2.40	22,100
0.5 N.	1.97	4.66	21,900
1.0 N.	3.86	9.13	21,800

It will be observed that the critical increment is indistinguishable from that found for the hydrolysis of acetyl glycine and this in spite of the fact that the hydrolysis proceeds with greater difficulty.

The following table gives the values of the "reduced velocity" constants.

TABLE XII.

Concentration of HCl.	$k \times 10^6$ 80° C.	$a_{H^+}$	$a_{H_2O}$	$\frac{k}{a_{H^+}}$	$\frac{k}{a_{H^+} \times a_{H_2O}}$
0.25 N.	1.009	0.20	0.98	5.05	5.1
0.5 N.	1.97	0.39	0.975	5.05	5.2
1.0 N.	3.86	0.84	0.96	4.59	4.8

In presence of glycerol the following values for the observed unimolecular velocity constants at 80° and 90° C. were obtained. In this case 1.0 N. Hydrochloric acid was employed in order to get more easily measurable values. The table contains also the critical increment and the "reduced velocity" values at 80° C.

As in the case of the acetyl compound the presence of glycerol causes a gradual increase in the velocity constant. The critical increment remains unchanged. Of the reduced velocity expressions it is evident that the greater degree of constancy is exhibited by  $\frac{k}{a_{H^+} \times a_{H_2O}}$ .

TABLE XIII. CONCENTRATION OF HYDROCHLORIC ACID 1.0 N.

Grams Glycerol Per 100 C.cs. Solution.	$k \times 10^6$ 80° C.	$k \times 10^6$ 90° C.	E in Calories.	$a_{H^+}$	$a_{H_2O}$	$\frac{k_{80}}{a_{H^+}}$	$\frac{k_{80}}{a_{H^+} \times a_{H_2O}}$
0	3.86	9.13	21,800	0.84	0.96	4.59	4.8
12.6	4.08	9.62	21,800	0.92	0.94	4.43	4.7
31.5	4.24	10.00	21,800	1.05	0.89	4.03	4.5
50.4	4.57	10.83	22,000	1.21	0.81	3.77	4.65

*The Hydrolysis of Benzoyl Glycine by 1.0 N. Hydrochloric Acid in Presence of Propyl Alcohol.*

The velocity constants and subsidiary data are given in the following table:—

TABLE XIV. CONCENTRATION OF HYDROCHLORIC ACID 1.0 N.

Grams Propyl Alcohol Per 100 C.cs. Solution.	$k \times 10^6$ 80° C.	$k \times 10^6$ 90° C.	E in Calories.	$a_{H^+}$	$a_{H_2O}$	$\frac{k_{80}}{a_{H^+}}$	$\frac{k_{80}}{a_{H^+} \times a_{H_2O}}$
0	3.86	9.13	21,800	0.84	0.96	4.59	4.8
8.08	5.62	12.67	22,000	0.93	0.95	6.04	6.35
20.2	4.62	10.94	22,100	0.87	0.94	5.31	5.6
32.3	4.10	9.79	22,300	0.795	0.925	5.15	5.6

As in the case of acetyl glycine the maximum still persists, but in the last column it is very much flattened.

The behaviour of benzoyl glycine in presence of varying amounts of potassium chloride with hydrochloric acid as the catalyst was substantially the same as that observed in the case of acetyl glycine, and consequently the actual data are omitted. It may be added that the critical increment shows even a greater apparent constancy than that exhibited in Table IX., no trend (however slight) in an upward direction being observable.

It is necessary to conclude in the case of both substituted glycines that the remarkably slow rate of decomposition (in view of the relatively low value of E) is due to a very small concentration of the actual reactant. This in turn points to the actual reactant being a complex of the substituted amino acid molecule + hydrogen ion which reacts at measurable speed with the monohydrol present in the solution.

**Solubility Relations of Acetyl Glycine and Benzoyl Glycine in Water-Glycerol Mixtures.**

Although it is recognised that the results already quoted are insufficient to afford all the information which is necessary for a satisfactory understanding of the hydrolysis of the peptide linkage, the general nature of the results so far obtained suggests that the activity of the substituted amino acid—the term which should logically enter into any “activity” theory of chemical change—is a quantity which does not differ markedly from the ordinary volume concentration. If this were not the case, it is difficult to see how the results obtained with different amounts of organic displacing agents, such as glycerol and propyl alcohol, would have shown the degree of comparability which they do show, the ordinary volume concentration terms for the substituted glycine being employed. Thus any attempt to use molar

fractions, for example, in such cases, would not lead even to approximate constancy for the "reduced velocity"  $\frac{k}{a_{H^+} \times a_{H_2O}}$ . With the object, how-

ever, of getting further information on this point, solubility determinations of acetyl glycine and benzoyl glycine have been carried out with the expectation that such values might afford a mode of calculation at least approximately correct of the activity of the substituted amino acid reactant. The marked dissimilarity in behaviour in respect of solubility shown in the following table necessitates the rejection of this mode of treatment. The difference in behaviour is all the more remarkable in view of the close similarity in respect of the kinetics of decomposition of both bodies. It is for this reason that the velocity data for the benzoyl derivatives have been quoted in addition to those for the acetyl glycine. The solubilities are expressed in grams per 100 c.c. of solution.

TABLE XV. TEMPERATURE 25° C.

Solvent: Water Containing	Solubility of Acetyl Glycine.	Solvent: Water Containing	Solubility of Benzoyl Glycine.
0.25 N. HCl	5.02	0.25 N. HCl	0.370
0.5 N. HCl	4.84	0.5 N. HCl	0.358
1.0 N. HCl	4.69	1.0 N. HCl	0.342
0.5 N. HCl + 12.6 per cent. glycerol }	3.98	1.0 N. HCl + 12.6 per cent. glycerol }	0.438
0.5 N. HCl + 31.5 per cent. glycerol }	3.46	1.0 N. HCl + 31.5 per cent. glycerol }	0.562
0.5 N. HCl + 50.4 per cent. glycerol }	3.01	1.0 N. HCl + 50.4 per cent. glycerol }	0.812

### Summary.

1. The hydrolysis of acetyl glycine using hydrochloric acid of various concentrations has been measured at 60° and 70° C. in aqueous solutions. Similar measurements have been carried out in solvents consisting of mixtures of water and glycerol, water and propyl alcohol, and water and KCl. Satisfactory unimolecular velocity constants were obtained in all cases.

2. Analogous measurements have been carried out with benzoyl glycine at the temperatures 80° and 90° C.

3. Under all the conditions examined the critical increment of activation is found to be 22,000 calories, the same for both substituted amino acids.

4. Although it is not possible to state quantitatively the molecular mechanism of the processes involved, the results obtained indicate that the activity of the hydrogen ion and of the water are involved, in all cases except where a strong electrolyte such as KCl is present. In the latter case the activity theory becomes quite inapplicable.

5. The solubility of the two substituted amino acids in water + glycerol + HCl mixtures has been determined. The addition of glycerol diminishes the solubility of acetyl glycine whilst it increases the solubility of benzoyl glycine.

Part of the expenses of the investigation were defrayed out of a grant made by Messrs. Brunner, Mond and Co., to the Department of Physical Chemistry of the University of Liverpool, for which grateful acknowledgment is made.

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The University of Liverpool.*

# A NEW METHOD OF MEASURING OVERVOLTAGE.

BY L. J. P. BYRNE.

(Communicated by SIR ROBERT ROBERTSON.)

(Received 27th July, 1927.)

When an electrolyte is submitted to electrolysis the potential difference between the electrodes,  $E$ , is composed of two distinct portions: (1), the ohmic potential fall due to the passage of the current along the column of electrolyte and (2), a pure *E.M.F.* effect at the electrodes. The latter is the sum of the overvoltages at the two electrodes. If the current flowing be  $I$  amperes and the ohmic resistance of the cell  $R$  ohms then the total overvoltage is  $E - IR$  volts. In the method described here these three quantities are measured. Briefly, the cell is placed in an alternating current bridge by means of which its resistance is measured; the polarising source is isolated by means of chokes possessing a very high impedance at the frequency used in the bridge yet presenting but a low resistance to direct currents. The ammeter is placed in this circuit while the *P.D.* across the cell is measured by means of a very high resistance voltmeter. Thus all three measurements can be made simultaneously while the current is actually flowing, giving overvoltages with a degree of certainty never previously attained. The method can be used at any current density. The arrangement is shown diagrammatically in Fig. 1. Switches, details of the A.C. source, the detector and the ammeter and voltmeter are omitted.

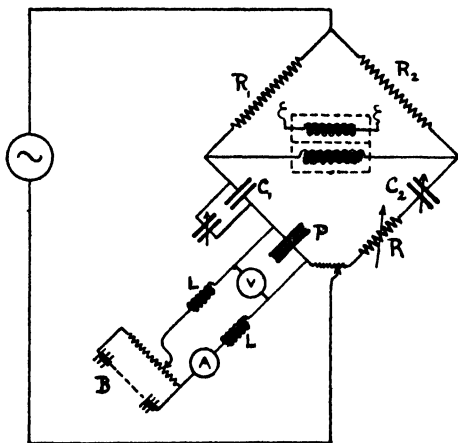


FIG. 1.— $P$ , electrolytic cell;  $R_1$  and  $R_2$ , ratio arms,  $R$ , balancing resistance of the bridge;  $C_1$  and  $C_2$ , condensers used to keep direct currents out of the network,  $V$ , a high resistance voltmeter ( $10^6$  ohms)  $A$ , an ammeter,  $B$ , the polarising source;  $L$ , chokes used to isolate  $B$  from the bridge.

The most satisfactory type of A.C. bridge has been found to be that described by Englund.<sup>1</sup> Its main feature is the elaborate shielding used. Alternating current of any frequency is supplied by a low-power valve oscillator. The detector is a three-stage transformer coupled valve amplifier and loud-speaker giving an amplification of some 20,000; this is necessary since the alternating current in the cell must be kept as small as possible. Good results have been obtained with a current of  $0.25 \times 10^{-4}$  ampere giving across a 200 ohm cell 0.005 volt r.m.s. A frequency of

<sup>1</sup> *Proc. Instit. of Radio Engineers (America)*, 8, 326 (1920).

2000 cycles/second was used; at this frequency a small choke presents a high impedance while shunt capacity effects are still small. Two 20-henry iron core chokes were used with an impedance of 250,000 ohms giving an error in the cell resistance of less than 1 part in 2000. The cross-section of the iron cores was great enough to avoid any possibility of saturation with the largest direct currents used, while the copper cross-section was chosen so as to be capable of dissipating the large amount of heat evolved. It should be noted that a very high *E.M.F.* is generated at the moment of breaking choke circuits if a large current is flowing.

The best source of potential for polarising the cell was found to be an accumulator battery (150 volts). This was allowed to deliver current at a few amperes to a resistance from which the required potentials were tapped. Since the D.C. resistance of the chokes was some 300 ohms a large excess

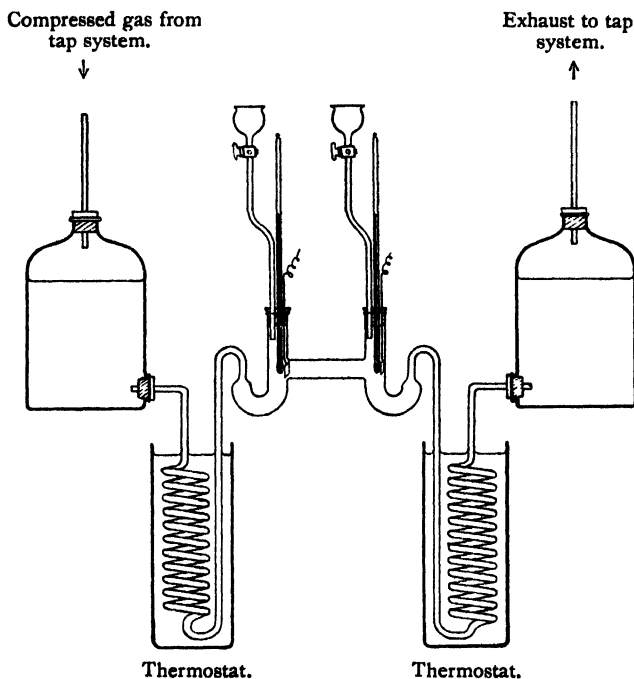


FIG. 2.—Electrolytic cell and circulatory apparatus (cell about  $\frac{1}{3}$  full size).

potential above that across the cell was necessary. To measure the potential across the cell a "potentiometer" arrangement was used. A high resistance of some  $10^6$  ohms was shunted across the cell and a number of tappings (1 to 20 ohms) taken at the low potential end; then the potentials across these were measured by a potentiometer in which the current could be varied within very wide limits. The ratios of the voltages across the tappings to the total applied *E.M.F.* were accurately determined. Calibration for each reading was obtained by switching a standard cell in place of the electrolytic cell and breaking the choke circuit. The effect of this system on the measured cell resistance was exactly known from the value of the shunt resistance.

The current was measured by taking the voltage drop across calibrated series resistances to the same potentiometer. As null indicator a high resistance suspended coil instrument was used in conjunction with a

telescope and illuminated scale. It would have been far preferable to use this as a direct-reading voltmeter but unfortunately very few D'Arsonval galvanometers will give a thirty degree deflection with even 1 per cent. accuracy owing to torsional fatigue and magnetic material in the coil. A voltage range of from 0.1 volt (full scale, *i.e.* 1000 divisions) to 200 volts (full scale) and a current range of from 1 milliampère to 1 ampère (each full scale) were obtained with an accuracy of 1 in 2000. The necessity for such high accuracy is readily seen from an example. If 0.3 ampère is flowing through a 200 ohm cell the voltage drop will be 60 volts. If the overvoltage is 2 volts, then 62 volts must be measured with an accuracy of 1 in 600 to give 5 per cent. accuracy on the overvoltage. Similarly the current and resistance must each be measured to 1 in 600 if only one of the three is liable to error, *i.e.* each must be measured to at least 1 in 1800 to give the overvoltage to 5 per cent. As, however, overvoltage is not a linear function of the current density, evidently the necessary accuracy will be less at low densities when the overvoltage is a large fraction of the total *P.D.* measured.

The cell was kept outside the thermostat and the electrolyte circulated through it and a spiral in the thermostat by means of compressed gas from a cylinder. To avoid shunting the cell by having a complete circle of liquid, an open circuit with a reservoir at either end was used, and the liquid forced shuttle-wise backwards and forwards. In this way earth capacity effects were minimised while the cooling and stirring obtained were such that even with 0.3 ampère through a 200 ohm cell the temperature rise was only 0.1° C. The cell (Fig. 2), was an H-shaped tube of pyrex glass of about 1.5 cm. internal diameter. Two 1 litre bottles and two spirals were used and by means of a system of three-way taps (Fig. 3), electrolyte was forced from one bottle through the spiral in the thermostat, through the cell, through the other spiral into the other bottle. Then the cycle was reversed. The cell was provided with a thermometer and stoppered funnel at each end.

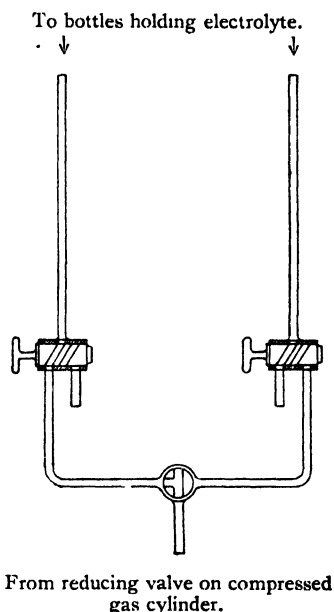


FIG. 3.—Tap system for reversing electrolyte flow.

## Results.

The method was used to show how overvoltage varies with current density.

Figs. 4, 5, and 6 show the relation for copper electrodes in neutral and acid copper sulphate solutions of various concentrations. Fig. 7 is for platinised platinum in sulphuric acid solutions. Figures for smooth platinum were obtained, but they show too great variation to be of much value. The resistance is difficult to determine in this case.

The figures given are always averages of a large number of separate determinations which sometimes varied considerably between themselves. The reason for this experimental error was that the three readings required

for any given determination were made consecutively by a single operator and small changes in the conditions were unavoidable. Normally three operators would be needed when the results would be unaffected by small changes in the current.

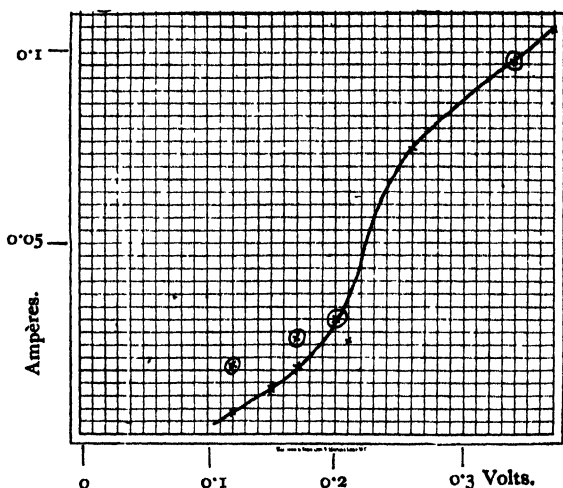


FIG. 4.—Relation between total overvoltage and current in neutral copper sulphate solution (68.7 g.  $\text{CuSO}_4$  per litre). Copper electrodes of about equal area. Temperature =  $24.5^\circ$  to  $25^\circ$  C. Resistance of cell = 200 to 210 ohms. The observations in circles were made on a different day from the others.

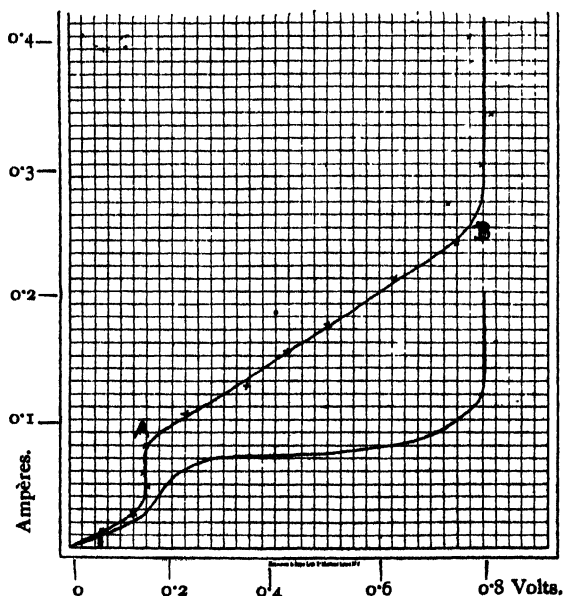


FIG. 5.—Relation between total overvoltage and current for copper electrodes of constant area in acid copper sulphate solution. ( $\text{CuSO}_4$ , 63.4 g./litre.  $\text{H}_2\text{SO}_4$ , 27.2 g./litre, 0.555 N.) Fig. 6 is reproduced without points for comparison. Temperature =  $24.5^\circ$  to  $25^\circ$  C. Resistance of cell = ca. 42 ohms.

The overvoltages shown are the combined effect of both electrodes; separate voltages could be obtained by making the two electrodes of very different areas.

The overvoltage is plotted against the current, but the latter is proportional to the current density since copper electrodes of the same area (*ca.* 0.5 cm.<sup>2</sup>) were used for all the copper experiments, and the same platinum electrodes (each side = *ca.* 1 cm.<sup>2</sup>) for all the sulphuric acid determinations. The range of currents employed is far greater than any small change in electrode area. The direction of the current was frequently reversed for the copper electrodes, but was kept constant for the platinum

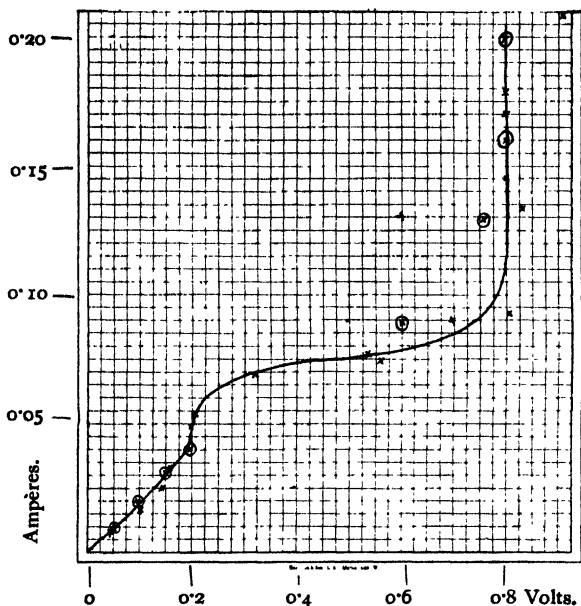


Fig. 6.—Relation between total overvoltage and current for copper electrodes of constant area in acid copper sulphate solutions.

$\text{CuSO}_4 = 35.0$  g./litre.  $\text{H}_2\text{SO}_4 = 13.8$  g./litre, 0.282 N.

Temperature 24.5 to 25.0° C. Resistance of cell = *ca.* 73 ohms.

$\text{CuSO}_4 = 19.7$  g./litre.  $\text{H}_2\text{SO}_4 = 6.5$  g./litre, 0.133 N.

Temperature 24.5° to 25.0° C. Resistance of cell = *ca.* 118 ohms.

electrodes. No definite relation could be detected between overvoltage and the relative directions of the current and electrolyte circulation.

### Electrolysis of Copper Sulphate Solutions.

Hydrogen always began to be evolved once the region of higher constant overvoltage (*e.g.* B, Fig. 5) was reached. This, however, in no way affected the bridge circuit nor was there any consistent change in resistance. As the current was increased beyond this point there was a great tendency for oxygen to be suddenly evolved as well. This was accompanied by great variations of the current, overvoltage, and resistance, the current being sometimes reduced almost to zero instantaneously and then recovering. This was always shown by a very loud rattling noise in the detector in the bridge—due to rapid variations of the polarising current. This lasted for a minute or so; then if the density were high enough hydrogen

and oxygen were evolved concurrently with solution and deposition of copper. At lower densities oxygen evolution would stop almost immediately and the overvoltage would drop to the higher constant figure (0.8 volt). At high densities a sudden interruption of the circulation always sent the electrolysis over to the unstable state. Overvoltages as high as 8 volts were observed sometimes in this unstable condition.

In the case of neutral copper sulphate hydrogen was not evolved alone but the unstable state set in at a far lower current density, *i.e.* the presence of sulphuric acid actually allows a considerably higher current to be used before the deposition of copper becomes inefficient. This is contrary to the view often expressed that acid facilitates the hydrogen-oxygen evolution.

### Electrolysis of Sulphuric Acid

The general trend of these curves is already well known. Gases are evolved as soon as the current begins, *e.g.* at 0.7 volt for curve I, Fig. 7. No effect on the resistance due to gas evolution could be found even though the electrode appeared to be covered with bubbles. The resistance changed, however, when gassing was so vigorous that a large portion of the solution was replaced by gas bubbles.

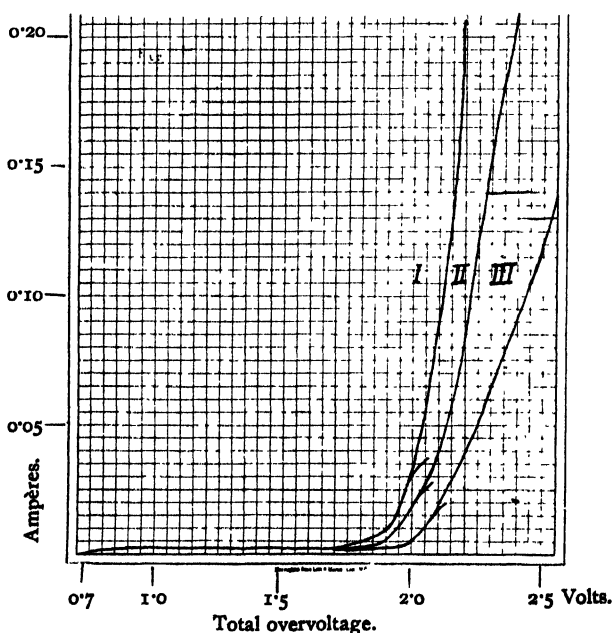


FIG. 7.—Relation between overvoltage and current for platinised platinum electrodes of constant area in dilute sulphuric acid. Temperature = 24.5° to 25° C.

- |   |  |
|---|--|
| I. $\text{H}_2\text{SO}_4 = 19.8 \text{ g./litre, } 0.404 \text{ N.}$   | Resistance of cell = <i>ca.</i> 59.5 ohms. |
| II. $\text{H}_2\text{SO}_4 = 7.79 \text{ g./litre, } 0.159 \text{ N.}$  | Resistance of cell = <i>ca.</i> 139 ohms.  |
| III. $\text{H}_2\text{SO}_4 = 4.66 \text{ g./litre, } 0.095 \text{ N.}$ | Resistance of cell = <i>ca.</i> 224 ohms.  |

(See Fig. 7.—Curve III.)

Current.	Overvoltage.	Current.	Overvoltage.	Current.	Overvoltage.
<i>Ampères</i>	<i>Volts</i>	<i>Ampères</i>	<i>Volts</i>	<i>Ampères</i>	<i>Volts</i>
0'00179	1'472	0'0437	2'22	0'136	2'30
'00251	1'924	'0575	2'16	'152	2'61
'00523	2'00	'0763	2'36	'162	2'39
'0092	2'04	'0927	2'38	'173	2'61
'0126	2'06	'101	2'35	'186	2'65
'0168	2'03	'111	2'37	'215	2'78
'0180	2'12	'126	2'59	'230	2'72
'0277	2'14	'128	2'39	'267	2'90
'0363	2'18				

An interesting practical corollary to the curves is the possibility of using alternating current for the preparation of hydrogen and oxygen gases. Obviously if a direct current potential of about 2 to 2.5 volts is applied to a suitable cell, an alternating current of 4 to 5 volts peak value can be used for producing electrolysis; the D.C. potential has to provide only the small current corresponding to the horizontal part of the curves. The effective slope of the curves depends of course on the resistance of the cell. The difficulty is the power supply. Either the D.C. biasing source must carry the whole A.C. supply, which defeats the object of the scheme, or the D.C. source must be isolated by means of an expensive filter circuit.

### Theoretical Considerations.

As regards the accuracy of this method there is only one point to consider. This is the method of determining the resistance. In the first place, in those parts of the curves where the curvature is great, the alternating current method will give a somewhat high result, depending on the magnitude of the current. Hence unless the A.C. in the bridge is very small, the overvoltages will be too low in regions where the change is non-linear. Secondly the method would not show the existence of a resistance which varied with the current. It seems unlikely, however, in view of the magnitude of the overvoltages obtained that such an effect can exist.

There are evidently a number of very suggestive points about these curves, and a short analysis will show that they could not reasonably be predicted on any of the current theories of electrode potential. Actually this work constituted a part of a long paper, in which, together with some work on contact potentials, it formed the basis of an attempt to develop a comprehensive theory of electrode potential and electrolysis. This theory, however, appeared to be unnecessary. This is the only apology that can be offered for adding yet another set of unexplained data to the mass that already encumbers physical chemistry.

### Summary.

A new method of measuring overvoltage has been described and illustrated. This method has been shown to give the true overvoltage existing during electrolysis without introducing any extraneous factors, and to be applicable over a very wide range of current density.

This work was carried out at the Government Laboratory by permission of the Government Chemist, Sir Robert Robertson, K.B.E., F.R.S., to whom thanks are due, as also for his continuous and helpful interest. Gratitude is also felt towards Dr. J. J. Fox, O.B.E., without whose very practical help and interest the work could hardly have been carried through.

# THE FREE ENERGY OF TRANSITION IN THE SYSTEM CALCITE-ARAGONITE.

By J. L. BUCHAN.

Communicated by PROFESSOR F. G. DONNAN.

Received 3rd August, 1927.

The problem of the evaluation of the free energy of transition in the system Calcite-Aragonite has been attempted several times, but the discord among the results of the various investigators seems to indicate that no satisfactory method has yet been devised. The most important of the results already obtained are given in Table I.

TABLE I.

Temperature.	$\frac{K_a}{K_c}$ .	$\Delta F$ , Cals./Gm. Mol.	Reference.
0° C.	1.8	377	Kohlrausch, <i>Z. physikal. Chem.</i> , <b>12</b> , 239, 1893, and <b>44</b> , 237, 1903. From specific conductance of saturated solution in pure water.
18° C.	1.7	362	
25° C.	1.7	371	
34° C.	1.6	339	
8° C.	1.52	276	Foote, <i>Z. physikal. Chem.</i> , <b>33</b> , 751, 1900. From specific conductance in water saturated with carbonate and with CO <sub>2</sub> at one atmosphere.
25° C.	1.44	255	
41° C.	1.40	248	
48° C.	1.37	237	
25° C.	1.35	208	Foote, <i>Z. physikal. Chem.</i> , <b>33</b> , 1900. From the equilibrium— $\text{CaCO}_3 + \text{K}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{CaC}_2\text{O}_4 + \text{K}_2\text{CO}_3$
49.7° C.	1.36	233	
50° C.	1.24	168	
18° C. ?	1.35	205	Seyler and Lloyd, <i>J.C.S.</i> , <b>95</b> , 1347, 1912.
25° C.	1.21	133	Kendall, <i>Phil. Mag.</i> , <b>23</b> , 958, 1912.
50° C.	1.24	163	
100° C.	1.22	174	
0° C.	1.16	95	Wells, 1915.
10° C.	1.17	104	
20° C.	1.17	108	
30° C.	1.19	124	
40° C.	1.24	158	
9° C.	1.33	160	Backstrom, <i>Z. physikal. Chem.</i> , <b>97</b> , 179, 1920. From specific conductance of saturated solution in water also saturated with CO <sub>2</sub> at constant pressure.
25° C.	1.382	191	
35° C.	1.434	220	

It was hoped that, by the electrometric method described below, it would be possible to obtain results at temperatures below 0° C., and thus derive a curve which it would be justifiable to extrapolate to the transition temperature. This hope was not realised, it being found increasingly

difficult to obtain reproducible values as the temperature was lowered. Other disturbing influences also were noticed, and will be found discussed briefly later.

*Experimental.*—The following cell was set up:—

Platinum saturated with hydrogen.	Saturated solution of calcite in 0.1 N. KCl containing 25 per cent. alcohol.	KCl solution as before.	Saturated solution of aragonite in KCl as before.	Platinum saturated with hydrogen.
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A mixture of hydrogen and carbon dioxide of constant composition and pressure was circulated continuously through the electrode vessels by means of an electromagnetic circulator of the form described by I. R. McHaffie<sup>1</sup> In each electrode vessel calcium hydrogen carbonate was formed in an amount depending upon the solubility of the particular form of calcium carbonate with which the solution was in contact. The  $\text{HCO}_3^-$  ions to which this bicarbonate gave rise put back the dissociation of the carbonic acid which was also formed, so that a hydrogen ion concentration cell was obtained.

If  $E$  is the *E.M.F.* of this cell, then the free energy of transition at that temperature is given by:—

$$F = 2 \times E \times 23070 \text{ cal. per g. mol.}$$

The object of the KCl was to reduce the internal resistance of the cell and also, as practically the same solution was used throughout, to eliminate the liquid-liquid potentials. The alcohol was to prevent the solution from freezing, as it was hoped that it would be possible to make some measurements below  $0^\circ \text{C}$ . The  $\text{CO}_2$  which was absorbed was replaced from a reservoir, so that the pressure inside the apparatus was maintained constant at 760 mm.

This apparatus was placed in an electrically heated and controlled thermostat, giving a variation of not more than  $1/40^\circ \text{C}$ .

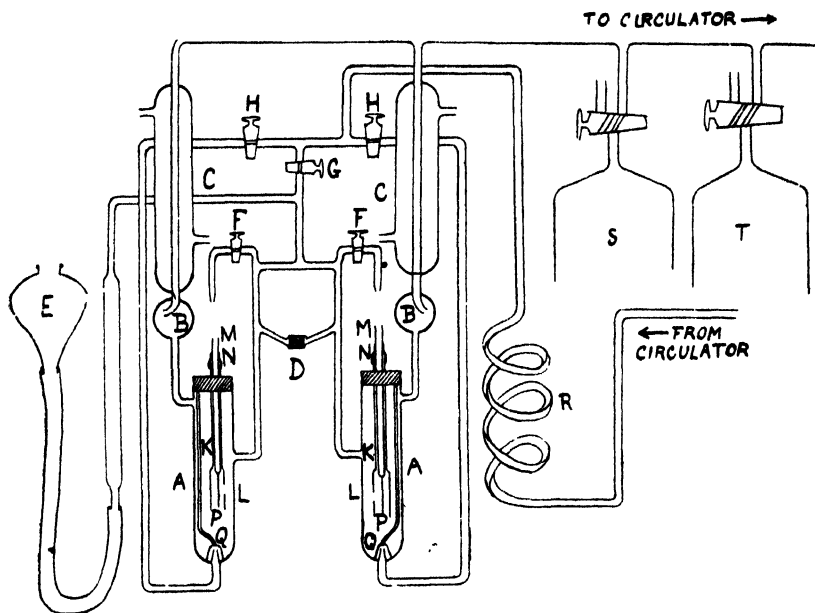
For these determinations it was necessary to prepare aragonite artificially, the natural product not being sufficiently pure. The method adopted was that described by Johnston, Merwin, and Williamson.<sup>2</sup> This consists of dropping slowly from burettes 0.1 N solutions of calcium chloride and potassium carbonate into about a litre of water kept at between  $85^\circ$  and  $90^\circ \text{C}$ ., and stirred continuously. In this way about one gm. of aragonite could be precipitated per hour. The product was very pure containing only a trace of calcite: also the crystals were remarkably uniform in size, and none of them small enough to give an enhanced solubility. To obtain suitable calcite was more difficult. At first crushed Iceland Spar was used, but it was found that no matter how carefully this was ground there was always a considerable number of very small particles formed, many indeed of a diameter less than  $2\mu$ , as found by microscopic examination, and it has been shown by Backstrom<sup>3</sup> that in crystals of this size the surface effect on the solubility cannot be ignored. It has been maintained by this author that these small particles can be removed by flotation, but this was found to be exceedingly difficult to effect, if indeed it were possible at all, for these small particles adhered to the larger ones by capillarity even after prolonged washing, so it is suspected that some of these remained in the final product.

<sup>1</sup> *Phil. Mag.*, March, 1926, p. 561.

<sup>2</sup> *J. Amer. Chem. Soc.*, 41, 473, 1916.

<sup>3</sup> *Z. physikal. Chem.*, 97, 179, 1920.

The next method tried was slow precipitation as in the case of aragonite, but this time at room temperature, about 20° C. The product was found to consist of aggregates of small crystals of calcite, many of them smaller than the necessary size. A number of these aggregates were hexagonal, the angles corresponding roughly to those of calcium carbonate hexahydrate,



- A.A. Electrode vessels. B.B. Splash heads. C.C. Condensers.  
 D. A plug of asbestos made between two Gooch plates. This permitted electrical contact between the two solutions, but prevented any passage of crystals from one vessel to the other.  
 E. A mercury reservoir, by the lowering of which the liquid was sucked up from the electrode vessels and made contact across D.  
 F.F. Taps, used for the introduction of the electrolyte into the vessels by suction.  
 H.H. Taps, by which the flow of gas through each electrode vessel was regulated.  
 K.K. Tubes carried by the rubber stoppers closing the electrode vessels. They are wider at the lower end where there is a hole L.L. in the side.  
 M.M. The tubes through which are fused the platinised platinum electrodes P.P. These tubes fit inside the tubes K.K., to which they are joined by rubber tubing N.N. The holes L.L. ensured that the platinum was always half immersed in the liquid, no matter at what distance below the surface the electrodes were placed. This gave more rapid saturation. When it was required to test the electrodes, the pressure inside the apparatus was brought to slightly above atmospheric by altering the level of E., the tubes M.M. were then removed and replaced by glass rods of the same size. By this method no air entered the apparatus and only a very small quantity of gas mixture escaped.  
 Q.Q. Glass caps placed over the tips of the gas inlet tubes so that the bubbles of gas could keep the solids in suspension.  
 R. A spiral to bring the gas to the temperature of the thermostat before it entered the electrode vessels.  
 S. and T. Two reservoirs, one for gas mixture and the other for carbon dioxide.

so it is suggested that this substance is first formed and then decomposes to give calcite. If this is the case it would be impossible to obtain suitable calcite by this method. At lower temperatures the hexahydrate was certainly formed and was isolated and analysed. Finally, therefore, it was necessary to use powdered Iceland Spar, washed many times by flotation.

Microscopic examination of the solids in the electrode vessels after several weeks showed that none of the aragonite had been transformed into calcite; in neither case were there any crystals which would indicate the formation of a hydrate of calcium carbonate, several of which have been reported. The same result was obtained by analysis. This, however, was not very definite, as there were many small crystals or cleavage fragments whose form could not be determined, while a small amount of hexahydrate, sufficient to alter the calcium carbonate content of the solution, would not be indicated by the analysis. Some of these cleavage fragments were smaller than in the original sample, showing that the gas stream had had a pulverising effect on the solids, an effect which has been observed by other workers. None of these particles, however, appeared to be of a size sufficiently small to give an enhanced solubility.

The potentiometer used was supplied by the Cambridge and Paul Instrument Co., and was capable of measuring to  $1 \times 10^{-5}$  volts, the galvanometer and connections being such that this *E.M.F.* gave a deflection of the spot of light of about 1 cm. on the scale.

Several difficulties had to be overcome before the final design of the apparatus was arrived at. The chief of these, one which could not indeed be eliminated entirely, was the poisoning of the electrodes. At first a mercury Sprengel pump had been used to circulate the gas mixture, but it was found that a deposit of mercury rapidly formed on the platinum electrodes, poisoning them. This poisoning effect was practically eliminated when the electromagnetic circulator was introduced. As, however, several days of continuous streaming of gas were required before the solutions became saturated, it was found advisable to introduce the electrodes into the vessels only when about to make a reading: this being the more necessary as the *E.M.F.* to be measured was so small. The electrodes, having only a small area, became saturated with hydrogen in a few minutes, giving an *E.M.F.* which remained constant for about five minutes, after which time the poisoning effect was noticed, and the electrodes had to be removed, cleaned and replatinised.

The cell was fitted up several times, always using new samples of the various reagents, and each time the same value was found for the *E.M.F.* The electrode dipping into the solution saturated with respect to calcite was found to be positive, and the *E.M.F.* at  $25^{\circ}$  C. to be 0.009 volts, with a variation of not more than  $\pm 0.0002$  volts during each experiment or between the different experiments.

This shows that the free energy of transition of aragonite into calcite is  $-414$  cal. per g. mol. at  $25^{\circ}$  C., a result which is in agreement with the value given by Kohlrausch, and also with that obtained from a consideration of the crystal structure, as will be shown in a later paper.

The various causes for any uncertainty have been mentioned, but the reproducibility of the result seems to show that these have been overcome.

In conclusion, the author wishes to express his indebtedness to Professor F. G. Donnan and also to Dr. A. E. Mitchell, for their interest and help during the carrying out of this work, and the preparation of the subsequent paper.

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# THE FREE ENERGIES OF SOLID COMPOUNDS, DEDUCED FROM THEIR CRYSTAL STRUCTURE: WITH SPECIAL REFERENCE TO CALCITE AND ARAGONITE.

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The simplest lattice from which the crystal can be built up by a process of repetition is considered, and the ions taken as point charges. This method can, of course, be looked upon only as an approximation. It would be necessary to consider every electron in each ion of the lattice in order to obtain a strictly accurate result, so that even if the various orbits, and their energies, were known, the calculation would be most laborious. How far these approximations are justified will be seen from the results.

The force acting between any two ions is taken as being given by Sir J. J. Thomson's formula—

$$F = \frac{E_1 \cdot E_2}{D a^2} \left( 1 - \frac{K}{a} \right) \quad . \quad . \quad . \quad (1)$$

where  $E_1$  and  $E_2$  are the charges on the ions,  $a$  the distance between them,  $D$  the dielectric constant of the medium, and  $K$  a constant depending upon the ions under consideration. Now if we integrate (1) between the limits  $d$  and  $\infty$ ,  $d$  being the distance between the two ions considered in the lattice, we obtain the work required to bring one ion into position when it is acted upon by only one other ion. This is—

$$\frac{E_1 \cdot E_2}{D \cdot d} \left( 1 - \frac{K}{2d} \right) \quad . \quad . \quad . \quad (2)$$

and so on for all the other ions required to form the lattice.

## Calcite.

X-ray measurements by W. H. and W. L. Bragg show that the crystal lattice is a regular rhomb, in which the smaller facial angle is  $78^\circ 6'$  and in which the perpendicular distance between the  $d_{100}$  faces is  $3.04 \text{ \AA}$ . Such a rhomb is shown below and it is seen that it has four  $\text{Ca}^{++}$  and four  $\text{CO}_3^{--}$  ions at alternate corners.

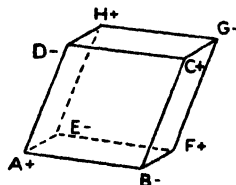


FIG. 1.

We then find by trigonometry the following lengths:—

$$\begin{array}{ll} AB = 3.174 \text{ \AA} & HB = 4.682 \text{ \AA} \\ AC = 5.336 \text{ \AA} & DF = 5.365 \text{ \AA} \\ DB = 3.441 \text{ \AA} & AG = 6.956 \text{ \AA} \end{array}$$

and we can see from the figure which other lengths are equal to these.

Now each ion is divalent, and each shares its charge with eight lattices, so for the purpose of building up one lattice we can write—

$$E_1 = - E_2 = \frac{2e}{8} = \frac{e}{4}$$

where  $e$  is the charge on a monovalent ion the accepted value of which is  $4.774 \times 10^{-10}$  E.S.U.

With the help of formula (2) we will now find the work required to bring up each ion from an infinite distance to its place in the lattice.

For A work = 0

$$\begin{aligned}
 B &= -\frac{e^2}{16D} \cdot \frac{1}{AB} \left(1 - \frac{K}{2AB}\right) \\
 C &= -\frac{e^2}{16D} \cdot \frac{1}{AB} \left(1 - \frac{K}{2AB}\right) + \frac{e^2}{16 \cdot D} \cdot \frac{1}{AC} \left(1 - \frac{K}{2AC}\right) \\
 D &= -\frac{2e^2}{16D} \cdot \frac{1}{AB} \left(1 - \frac{K}{2AB}\right) + \frac{e^2}{16 \cdot D} \cdot \frac{1}{DB} \left(1 - \frac{K}{2DB}\right) \\
 E &= -\frac{e^2}{16D} \cdot \frac{1}{AB} \left(1 - \frac{K}{2AB}\right) + \frac{2e^2}{16D} \cdot \frac{1}{DB} \left(1 - \frac{K}{2DB}\right) \\
 &\quad - \frac{e^2}{16D} \cdot \frac{1}{HB} \left(1 - \frac{K}{2HB}\right) \\
 F &= -\frac{2e^2}{16D} \cdot \frac{1}{AB} \left(1 - \frac{K}{2AB}\right) + \frac{e^2}{16D} \cdot \frac{1}{DB} \left(1 - \frac{K}{2DB}\right) \\
 &\quad + \frac{e^2}{16D} \cdot \frac{1}{AC} \left(1 - \frac{K}{2AC}\right) - \frac{e^2}{16D} \cdot \frac{1}{DF} \left(1 - \frac{K}{2DF}\right) \\
 G &= -\frac{2e^2}{16D} \cdot \frac{1}{AB} \left(1 - \frac{K}{2AB}\right) + \frac{3e^2}{16D} \cdot \frac{1}{AC} \left(1 - \frac{K}{2AC}\right) \\
 &\quad - \frac{e^2}{16D} \cdot \frac{1}{AG} \left(1 - \frac{K}{2AG}\right) \\
 H &= -\frac{3e^2}{16D} \cdot \frac{1}{AB} \left(1 - \frac{K}{2AB}\right) + \frac{e^2}{16D} \cdot \frac{1}{AC} \left(1 - \frac{K}{2AC}\right) \\
 &\quad + \frac{2e^2}{16D} \cdot \frac{1}{DB} \left(1 - \frac{K}{2DB}\right) - \frac{e^2}{16D} \cdot \frac{1}{HB} \left(1 - \frac{K}{2HB}\right)
 \end{aligned}$$

and the work required to form the whole lattice is the sum of these terms. This is—

$$\frac{e^2}{16D} \left[ -\frac{12}{AB} \left(1 - \frac{K}{2AB}\right) + \frac{6}{AC} \left(1 - \frac{K}{2AC}\right) + \frac{6}{DB} \left(1 - \frac{K}{2DB}\right) - \frac{2}{HB} \left(1 - \frac{K}{2HB}\right) \right. \\
 \left. - \frac{1}{DF} \left(1 - \frac{K}{2DF}\right) - \frac{1}{AG} \left(1 - \frac{K}{2AG}\right) \right].$$

When we substitute the numerical values of AB etc. in the above and sum the various terms we obtain—

$$\frac{e^2}{16D} \left( -\frac{1.6683}{10^{-8}} + \frac{.3101 \cdot K}{10^{-16}} \right) \text{ E.S.U.} \times \text{cm.} \quad (3)$$

as the work required to form one lattice of calcite.

The value of D is different in different directions in a crystal, and there is some uncertainty in the literature as to the magnitude of these values. The method adopted in this case, and throughout this paper, is to take the average value of the dielectric constant. This in the case of Calcite is 8.5.

Now such a lattice, since it shares its ions with others, contains half a molecule, so that the free energy of formation of calcite per gm. mol. is—

$$\frac{4.774^2 \times 10^{-20}}{16 \times 8.5} \left( -\frac{1.6683}{10^{-8}} + \frac{.3101 \cdot K}{10^{-16}} \right) \times \frac{6.062 \times 10^{23}}{4.185 \times 10^7} \times 2 \text{ cal.} \quad (4)$$

this being, of course, for the formation from  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$ .

If then we can find the value of  $K$  the problem is solved. The expression (4) can be written in the form—

$$\frac{A}{d_{100}} \left( B - \frac{CK}{d_{100}} \right) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $d_{100}$  is the distance between those faces in the lattice and  $A$ ,  $B$  and  $C$  are numerical constants.

Also, for the formation of a slightly larger lattice in which  $d_{100}$  is increased to  $d_{100} + \delta d_{100}$  the work required is—

$$\frac{A}{d_{100} + \delta d_{100}} \left( B - \frac{CK}{d_{100} + \delta d_{100}} \right)$$

and as the lattice of calcite is stable the difference between these two values should be zero.

$$\therefore A \left[ \frac{1}{d_{100}} \left( B - \frac{CK}{d_{100}} \right) - \frac{1}{d_{100} + \delta d_{100}} \left( B - \frac{CK}{d_{100} + \delta d_{100}} \right) \right] = 0$$

$$i.e. A \left[ \frac{B(d_{100} + \delta d_{100}) - B d_{100} - \frac{CK}{d_{100}}(d_{100} + \delta d_{100}) + \frac{CK}{d_{100} + \delta d_{100}} \cdot d_{100}}{d_{100}(d_{100} + \delta d_{100})} \right] = 0$$

$$i.e. A \left[ \frac{B \cdot \delta d_{100} - \frac{CK(2d_{100} \cdot \delta d_{100} + \delta d_{100}^2)}{d_{100}(d_{100} + \delta d_{100})}}{d_{100}(d_{100} + \delta d_{100})} \right] = 0$$

$$i.e. A \left[ \frac{B \cdot d_{100} \cdot \delta d_{100}(d_{100} + \delta d_{100}) - CK(2d_{100} \cdot \delta d_{100} + \delta d_{100}^2)}{d_{100}^2(d_{100} + \delta d_{100})^2} \right] = 0.$$

We can neglect  $\delta d_{100}^2$  as an infinitesimal of the second order, and as  $A$  is not zero nor the denominator infinite we have—

$$B \cdot d_{100} \cdot \delta d_{100} - 2 \cdot C \cdot K \cdot d_{100} \cdot \delta d_{100} = 0$$

$$i.e. K = \frac{B \cdot d_{100}}{2C}.$$

Now we see from (4) and (5) that

$$\frac{B}{d_{100}} = -\frac{1.6683}{10^{-8}} \quad \text{and} \quad -\frac{C}{d_{100}^2} = \frac{.3101}{10^{-16}}.$$

Thus we have

$$K = \frac{1.6683}{10^{-8}} \times \frac{10^{-16}}{.3101} \times \frac{1}{2} \\ = 2.69 \times 10^{-8}.$$

We can now substitute this value of  $K$  in (4) when we obtain the free energy of formation of calcite from  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$  to be

$$- 4060 \text{ calories per g. mol.}$$

This being at  $18^\circ \text{C.}$ , the temperature of the X-ray measurements.

The free energy of formation of more than one lattice need not be considered, as the energy change when a number of them are brought together to form a crystal of ordinary size would be the free energy of crystallisation, which is very small compared with that of formation.

**Aragonite.**

W. L. Bragg has shown<sup>1</sup> that aragonite has a simple orthorhombic lattice of the following dimensions—

$$d_{100} = 2.47 \text{ \AA} \quad d_{010} = 3.97 \text{ \AA} \quad d_{001} = 2.86 \text{ \AA}$$

and this prism contains half a molecule.

Proceeding as in the case of calcite we obtain the free energy of formation of aragonite to be—

$$\frac{4.774^2 \times 10^{-20}}{16 \times D} \left( -\frac{2.0232}{10^{-8}} + \frac{.480}{10^{-16}} \cdot K_1 \right) \times \frac{6.062 \times 10^{23}}{4.185 \times 10^7} \times 2 \text{ cal. per g. mol.}$$

In this case we find the value of  $D$  to be  $8.21$ , so that we can evaluate the expression if we know  $K_1$ .

The value of  $K$  for calcite was found by making use of the fact that the lattice was stable, so that a small displacement of the ions would involve no energy change. This method, however, cannot be applied to aragonite, the lattice of which is not stable. As, however, these constants depend chiefly, if not entirely, upon the kind of atoms forming the compound, it seems reasonable to put  $K_1 = K$ . We can then make the substitutions for  $K_1$  and  $D$  in the above expression, when we obtain—

The free energy of formation of aragonite from  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$  is  
 — 3680 calories per g. mol. at  $18^\circ \text{C}$ .

From these values of the free energy of formation of calcite and aragonite we see that the former is the smaller. This means that at  $18^\circ \text{C}$ . (the temperature at which the crystal structure was determined) aragonite is unstable with regard to calcite, and this is in agreement with the literature on the subject. Further, this difference is seen to be 380 calories per g. mol. at  $18^\circ \text{C}$ ., and this is in good agreement with the figures in Table I. (previous paper) especially those of Kohlrausch, whose value at  $18^\circ \text{C}$ . is 362 cal./g. mol. This good agreement shows that the discrepancies between the two columns of Table I. are probably due to errors introduced when calculating  $\Delta F_{298}$  from  $\Delta H_{298}$  as will be shown later.

Now as these values for the free energy of calcite and aragonite are for the formation from  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$ , it is necessary to obtain the free energies of formation of these ions from the component elements in their standard states before we can compare our calculated values with those in the literature.

Lewis and Randall give the value of  $\Delta F_{298}$  for  $\text{CO}_3^{--}$  as — 12560 cal. per g. mol. The value for  $\text{Ca}^{++}$  is however more difficult to obtain, but we can calculate it from the value of  $\Delta H_{298}$  for this ion, which is given in the literature as — 109400 cal. per g. mol., and from the value of the entropy of electron gas. We have now enough data to calculate  $\Delta F_{298}$  for calcite from carbon, calcium, and oxygen, by combining the values of  $\Delta F_{298}$  for  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$  with that for calcite from these ions. We thus obtain  $\Delta F_{298} = 244,560$  cal. per g. mol. for the formation of calcite from its elements in their standard states. Also, from the literature, we know that  $\Delta H_{298}$  for calcite from its elements is — 270,000 cal. per g. mol. approximately and, if we know the values of the entropies of all the substances concerned, we can from this calculate  $\Delta F_{298}$  for calcite. Unfortunately these values are not known. They may, however, be calculated from a modification of Sackur's Equation, as deduced by Latimer.<sup>2</sup>

<sup>1</sup> *Proc. Roy. Soc. A.*, Jan. 1924.

<sup>2</sup> *J. Amer. Chem. Soc.*, 43, 818 (1921).

This is 
$$S_{298}^0 = \frac{3}{2}R \cdot \ln \cdot A - 0.94 \quad (\text{approx.})$$

where  $A$  is the atomic weight and  $0.94$  is an empirical constant. The sum of the individual values of  $S_{298}^0$  gives the entropy of the compound to about one entropy unit, according to Latimer. By this means we find that  $\Delta F_{298}$  for calcite from its elements is given in the literature as  $-258,910$  cal. per g. mol.

The difference between these two values of  $\Delta F_{298}$  is small considering the approximations used and the variations of  $\Delta H_{298}$  for the various substances given in the literature, *e.g.* there is a difference of  $15,000$  cal. per g. mol. between the value of  $\Delta H_{298}$  for calcite given by Thomsen and that given by Berthelot.

The free energies of other compounds have been calculated in the same way, and the results tabulated in Table I. It will be seen that in these cases, also, the agreement is satisfactory.

Great accuracy cannot of course be claimed for this method, but in most cases it gives a value within 5 or 6 per cent. of that obtained by thermo-chemical measurements. One of the principal causes for inaccuracy lies in the value taken for the dielectric constant, for the literature on this subject is rather discordant. The method, however, acts as a useful check, and, with improvement in the necessary data, it might rival the older thermo-chemical methods.

Here, also, the author wishes to express his thanks to Professor F. G. Donnan for his interest and advice during the preparation of this work.

TABLE I.

Substance.	$\Delta F_{298}$ from Crystal Structure.	$\Delta F_{298}$ from $\Delta H_{298}$ .
	Cals./g. mol.	Cals./g. mol.
Calcite . . . .	-244560	-258910
Aragonite . . . .	-244160	—
+ FeCO <sub>3</sub> . . . .	-151520	-175000
MnCO <sub>3</sub> . . . .	-183160	-198900
NaNO <sub>3</sub> . . . .	-94160	-92400
† NH <sub>4</sub> I . . . .	-32120	-29400
NaCl . . . .	-95200	-91790

† The value of the dielectric constant of FeCO<sub>3</sub> was taken to be the same as that for MnCO<sub>3</sub>.

‡ The dielectric constant of NH<sub>4</sub>I was computed from the values given for those of NH<sub>4</sub>Cl and NH<sub>4</sub>Br.

## REVIEWS OF BOOKS.

**Flame and Combustion in Gases.** By WILLIAM A. BONE and DONALD T. A. TOWNEND. (London: Longmans, Green & Co., Ltd. Pp. xvi + 548, with 30 plates and 162 figures. Price 32s.)

Since the time of Boyle, Hooke and Mayow, an extensive literature on flame and combustion has accumulated which has never been adequately summarised at any period of its growth. This literature has largely consisted of isolated publications describing the work of one man or of contributions to little known scientific journals, neither class of which is readily accessible to the student. Thus Davy summarised his own work on flame in 1818 in a monograph on the safety lamp which is rarely to be found in scientific libraries. Also, the collected papers of Bunsen, 1904, and of Mallard and Le Chatelier, 1875, have not been extensively circulated in this country. On the other hand, the work of Berthelot on explosives has been made readily accessible to English readers through the excellent translation of Hake and MacNab.

The more recent developments which have owed their inception to the work of Dixon and the school founded by him at Manchester had not been surveyed in any comprehensive manner until the appearance of the above volume by Bone and Townend.

The selection of those experimental facts and speculations which have most contributed to the development of research on flame and combustion and their presentation as a readable whole is a task of no mean order. The subject bristles with controversies, both active and quiescent, and an *ex parte* statement of these by men who are deeply immersed in the subject is wellnigh impossible. The authors have disarmed criticism on this point by admitting "the unconscious bias of an investigator to exaggerate the importance of those parts of the subject in which he himself is particularly interested." The authors say: "we have dealt chiefly with those aspects of the subject about which we know most at first hand."

The first section of the volume is a historical review beginning with the investigations of Boyle and ending with the researches of Bunsen, which period saw the development of our ideas as to the nature of flame, as well as the development of the technique necessary for experimental investigation. The account of this period given by the authors makes very interesting reading and omits little that is essential for the understanding of the trend of ideas. A complete bibliography of the earlier investigations on flame and combustion has yet to be made. The authors would add considerably to the value of their historical section if they could include such a summary in their book.

The initial phases of the explosion wave, the ignition temperatures, electrical ignition, the limits of self-propagation, flame speeds, the development of detonation and the measurements of rates of explosion are dealt with in the second section, at the end of which are appended chapters on stationary flames and on the radiation from flames. The third section is devoted to the phenomena observed during explosions in closed vessels, and the mechanism of gaseous combustion and surface combustion are treated in two further sections.

Sections II. and III., which form the body of the book, give a clear and lucid account of the development of an experimental technique, begun in the hands of Mallard and Le Chatelier and of Berthelot and Vieille and so ably developed by Dixon, Bone and Wheeler, and their colleagues. The photographic method of Mallard and Le Chatelier for the measurement of flame speeds is perhaps the

most striking example of the technique used by workers in this field. The photographs of the various phases of the explosion wave, which are often of great beauty, serve as permanent records of phenomena which are but imperfectly understood at the time they are obtained. They have led, however, to the accumulation of a mass of experimental material which is of direct service in the design of petrol engines, and which has increased safety in mines and in industries in which gaseous explosions are to be feared.

The authors have spared no pains in sorting out the most useful experimental data, which are presented in the form of figures and tables. These will make the book a valuable work of reference.

The chapter on radiation from flames is however open to criticism. No reference is made to the absorption spectra of the gases emitting the radiation; it is scarcely possible to treat adequately the emission from flames without taking into account the knowledge of absorption spectra gained in recent years. For example, the authors accept the statement of Julius that the  $4.4$  and  $2.8\mu$  bands emitted from the Bunsen flame are due to carbon dioxide and water molecules respectively, and that there is no emission by carbon dioxide at  $2.8\mu$ . This is not in accord with experimental fact, for both the flame and explosion of *dry* carbon monoxide and oxygen give a marked emission at this wave-length. In an explosion the intensity of emission at  $2.8\mu$  is even greater than at  $4.4\mu$ . This error would not have been made had the absorption spectrum of carbon dioxide been taken into account, which gives maxima at the same wave-lengths as the emission. One of the causes of the confusion lies in the fact that a water band coincides very nearly with a carbon dioxide band at  $2.7$  to  $2.8\mu$ .

One of the most interesting phenomena met with in gaseous explosions is the effect discovered by Dixon, that water or hydrogen accelerates the rate of combustion of carbon monoxide. The experimental work on this question is summarised in the fourth section of the book, which also contains an account of experiments on the vexed question of the mode of combustion of hydrocarbons. There is much that is controversial in both lines of work and the different points of view are clearly brought out. The experimental data recorded may well prove of great industrial importance in the conversion of hydrocarbons into their oxidation products. The researches on catalytic combustion, very widely studied by Bone and Wheeler in 1906 are described in Section IV., together with an account of previous work. A brief description is given of Langmuir's theories of catalysis with which the authors do not appear to be in sympathy. The work of Taylor and others receives a bare mention and that of a derogatory character.

The volume is a valuable contribution to the subject of flame and combustion. It is of greatest value when dealing with that portion of the field which has resulted directly from the development of the experimental technique of Chatelier, Berthelot, and Dixon. It also gives an excellent summary of the work of Bone and his co-workers. It is not so successful in its treatment of the recent developments in the field of kinetics with which the authors are not in sympathy.

The book is excellently printed and is in every way a valuable acquisition to one's library.

W. E. G.

**Electro-organic Chemistry.** By C. J. BROCKMAN. (New York: John Wiley & Sons, Inc. Pp. 381. Price \$5.00.)

This book is essentially a recapitulation of work already published in the field of electro-organic chemistry, but it is critical in nature. The study of the subject

has been carried out in an exhaustive manner and the nomenclature brought up-to-date. The compilation as a whole forms a very valuable addition to our literature and should serve as a reference book for many years to come.

The book commences with a brief history of the subject which is disposed of in a couple of pages. This section is unduly curtailed, and the matter dealt with later is important enough to have a more comprehensive history. The next section briefly describes the methods and apparatus employed by various investigators.

The author then passes to the essential part of his business, namely, the reactions which take place in the anodic and cathodic chambers of electrolytic apparatus. The book naturally falls into sections and is classified under the following titles: "Introduction to Electrolytic Oxidation," "The Oxidation of Ionized Substances, Parts I. and II.," "The Oxidation of Non-Ionized Substances, Parts I. and II.," "Substitution," "Introduction to Electrolytic Reduction," "The Reduction of Aromatic Nitro Compounds, Parts, I., II., III., and IV.," "The Reduction of Nitroso Compounds, etc.," "The Addition of Hydrogen to Unsaturated Compounds," "The Reduction of the Carbonyl Group," and "The Reduction of Compounds Containing Arsenic, Chlorine, Sulphur, Mercury, etc."

The above sections are discussed in detail and in a very readable manner. The subject is thoroughly treated, although at times undue weight is attached to work of minor importance. This is perhaps unavoidable, as the author has endeavoured to interpret fairly and impartially the results of all investigators.

The book throughout is copiously illustrated with graphs, graphic formulæ and equations, and no effort has been spared to elucidate clearly the various topics discussed.

The author is to be congratulated on presenting such a useful addition to existing literature. There is a growing necessity for comprehensive work of this type in which the whole range of past investigation has been considered, especially as it is frequently found that the old pioneer work on which modern discussion has been founded is apt to be overlooked and undue credit is assigned to later research workers.

H. D. L.

**A Dictionary of Applied Chemistry.** By Sir EDWARD THORPE, C.B., F.R.S. Vol. VII., Thalenite—Z. with Index to Vols. I. to VII. (London: Longmans, Green & Co., Ltd. Pp. viii + 610 with 155 pp., index. Price 60s. net.)

With the issue of this volume the great labour of producing the revised edition of this work is completed, Dr. Forster Morley being responsible for the final revision of the volume. The extent of the enlargement may be judged by the fact that the matter so far as it is reprinted, occupied only 380 pages in the last edition. Amongst the new contributions of special interest to members of this society is an article on the physical and chemical properties of water by H. V. A. Briscoe, the article on water originally appearing over the initials of P. F. Frankland now being reprinted practically without alteration on pp. 368 *et seq.* under the sub-title "Water in its Economic and Sanitary Relations—Drinking Water." The new article provides an excellent summary. A new article on Water Softening by Professor Briscoe and Dr. P. L. Robinson is also included. Slight additions have been made to the articles on thermometry and thermostats, chiefly in the way of adding to the lists of references.

Since the last edition appeared in 1913 there are as may be expected

additions to the articles on Thorium, etc. The articles on Vanadium and Tungsten have also been somewhat enlarged.

New contributors to the volume are F. H. Carr on Tropeines and Sir F. G. Hopkins on Vitamines. It is unsafe to assume, however, that the appearance of a new name as author of a subject treated in the previous editions, means that the article has been re-written, since it is clear the old text has been altered as little as possible, the new matter being introduced by way of supplements. Some articles have now acquired more than one such supplement and, although an admirable index is provided, the method of treatment does not in some cases make for clear reading. Moreover, the mode of reference has occasionally become out of date, *e.g.*, "the method just described has been patented (D. R. P. —, 1887)" is wholly unnecessary 40 years after the patent was granted. The warning was admirable when the process was in fact subject to patent rights, but if any such reference be now necessary for purely literary purposes, the patent number alone would suffice. However, the reader will doubtless console himself with the thought that if every article had been re-written the volume must have cost much more than £3.

**An Introduction to the Scientific Study of the Soil.** By NORMAN M. COMBER. (London, 1927: Edward Arnold & Co. Pp. 192. Price 7s. 6d. net.)

This interesting little book is intended primarily for students working for agricultural diplomas and degrees but, within the necessary limitations of space, the subject is expounded with such clarity that it cannot fail to be of interest to amateurs who wish to acquire some knowledge of the work which has been done in the chemists and physics of the soil. Three short appendices of three or four pages each are devoted to an explanation of the nature of Colloids, of Surface Tension and Capillarity, and of the Reaction of Aqueous Solutions; these are equally clearly expounded. An interesting feature is the elimination from the body of the book of references to the literature, the final chapter being devoted to a guide to the literature; in addition to critical reference to standard textbooks and periodicals there is a classified bibliography of the more important papers on various aspects of the subject.

**Spectroscopy.** Vol. III. By E. C. C. BALY. (Text-books of Physical Chemistry. London, Longmans, Green & Co. Ltd. Pp. viii and 532 with 6 plates. 22s. 6d. net.)

The third volume of this four-volume work on Spectroscopy deals with line spectra, the Zeeman and the Stark effects on line spectra, and with emission band spectra. Of the 520 pages some 50 pages only are devoted to the vast domain of molecular emission spectra,—an assignment of space which we venture to suggest is in no sense a just assessment of the relative importance and extent of our knowledge of such.

In Chapter I. dealing with series of lines in spectra, the author has adopted a historical presentation of the subject. We are therefore led through an account of the early work and ideas of Balmer, Kayser, Runge, Rydberg, and others, to the modern views on series relations. Interesting as this may be to the spectroscopist who is steeped in Bohr's theory and its developments, we feel it is a somewhat unsatisfactory approach for the student to whom the subject is new, and who approaches it as a physicist, not as a historian. It involves him in

constantly revising his ideas and views in the light of newer developments and leaves him continually groping for the features which may be permanent. To the beginner this process is laborious and mentally exhausting, and one which we do not favour.

The author has given an extensive account of line spectra and series relationships. The work of early investigators is described at length and is followed by an account of Hick's work, Bohr's theory, and Fowler's work on enhanced line series. The existence of multiplets in line spectra follows this and introduces the concept of the inner quantum number and the work of Catalan and others in this field. The work of Millikan and Bowen on the spectra of multiply ionised atoms is also included. We should also mention a brief but excellent account, contributed by Professor Ornstein, of the work of the Utrecht school on intensity relations in multiplets. This chapter deals with all the salient developments in the study of line spectra, and its 307 pages would in themselves make a fair sized book. We consider, however, that as a chapter for the student it would have proved equally useful at two-thirds of the length. As it stands it is too much a catalogue of numerical data for which the student will have no use, and for which the research worker will naturally turn to the original papers. This is particularly the case in connection with the multiplet structure of manganese, chromium, and iron. This overloading of the book with numerical data will be apparent from the existence of some 228 tables in its 520 pages.

Good representative accounts are given of the effects of electric and magnetic fields on spectral lines.

The chapter on band spectra is poor, and does no justice to the vast amount of work done, and the knowledge gained in this field in recent years. Judged, however, by the matter presented in some 50 pages it is still a poor chapter and contains a good deal that is obsolete. We mention a few examples. The old ideas of Deslandres are presented in some detail. The first and second positive nitrogen band systems are used by way of illustration, but the arrangements are those of twenty-five years ago, and no mention is made of the modern analysis of these systems. Space is devoted to what purports to be a "striking relationship" discovered by Deslandres of a fundamental frequency of  $1062\cdot5$  found in connection with all the band spectra of carbon, oxygen, and nitrogen! We refrain from further comment except to say that the idea is quite fantastic. Again, it is unfortunate to find old heresies still expounded, such as that the cyanogen bands are due to a nitrogen molecule ( $N_2$ ), and that the initial state of the red cyanogen group is the final state of the first positive nitrogen group. These ideas were exploded by Birge and others some time ago, and the precise relationships of all the nitrogen band spectra are known quite definitely. Some of the work of Curtis on the Helium band spectrum is quoted; no mention is made however of subsequent work by Kratzer and others, that alternate lines of the helium bands are now regarded as missing, that  $\frac{1}{2}$ -quantum numbers are to be uniformly replaced by  $\frac{3}{2}$ -quantum numbers, and that the moments of inertia are therefore really twice as large as given.

Several references are also made to positive, zero, and negative branches as Heurlinger's P, Q, and R branches. The order should of course be reversed.

We hope to find this chapter very different when a new edition of the book is called for.

R. C. J.

# Transactions of the Faraday Society.

## INDEX—VOLUME XXIII., 1927.

- Adair, G. S.** The activity coefficients of protein ions, p. 536.
- Allmand, A. J.** A note on the occurrence of points of inflexion in the concentration vapour pressure curves of aqueous solutions of certain electrolytes, p. 477.
- Allmand, A. J., and Burrage, L. J.** An electrometric study of the system potassium chloride—lead chloride and water at 25°, p. 470.
- Allmand, A. J. and Puttick, A.** The electrolytic oxidation of *para*-toluic acid in alkaline solution, p. 643.
- Bell, R. P.** See Hartley, H., and Bell, R. P.
- Bennett, J. A. J.** The electrical conductivity of vapours and liquid drops during incipient combustion, p. 295.
- Ionization in flames of various organic substances, p. 307.
- Bjerrum, N.** Some anomalies in the theory of solution of strong electrolytes and their explanation, p. 445.
- Bowden, F. B.** On the persistence of potential at a mercury cathode on open circuit, p. 571.
- Brönstead, J. N.** On the activity of electrolytes. (Introduction to General Discussion on "The Theory of Strong Electrolytes. Part 2. Activity"), p. 416.
- Buchan, J. L.** The free energy of transition in the system calcite-aragonite, p. 666.
- The free energies of solid compounds deduced from their crystal structure with special reference to calcite and aragonite, p. 672.
- Buckley, P. S.** See Wolfenden, J. H., Wright, C. P., Ross-Kane, N. L., and Buckley, P. S.
- Burdon, R. S., and Oliphant, M. L.** The problem of the surface tension of mercury and the action of aqueous solutions on a mercury surface, p. 205.
- Burrage, L. J.** See Allmand, A. J., and Burrage, L. J.
- Byrne, L. J. P.** A new method of measuring overvoltage, p. 660.
- Chapman, D. L.** Note on the interionic attraction theory of Debye and Hückel, p. 443.
- Chatterji, A. C., and Dhar, N. R.** Condition of silver chromate in gelatin from electric conductivity and diffusion experiments, p. 23.
- Corran, R. F.** The decomposition of triethyl sulphonium bromide in mixed solvents, p. 605.
- Cowperthwaite, I. A.** See MacInnes, D. A., and Cowperthwaite, I. A.
- Crennell, J. T.** See Lea, F. M., and Crennell, J. T.
- De Bruyne, N. A., and Sanderson, R. W. W.** The electrostatic capacity of aluminium and tantalum anode films, pp. 42 and 107.
- Debye, P.** Report on conductivity of strong electrolytes in dilute solution. (Introductory paper at General Discussion on "The Theory of Strong Electrolytes. Part 1. Mobility of Ions"), p. 334.
- Dhar, N. R.** See Chatterji, A. C., and Dhar, N. R.
- Downes, H. I., and Perman, E. P.** An improved method of measuring vapour pressure by air bubbling (vapour pressure and heat of dilution of aqueous solutions, Part 4), p. 95.
- Elder, L. W., and Rideal, E. K.** Thermal decomposition of  $H_2O_2$  vapour, p. 545.
- Elliott, G. A.** The activation of hydrogen in the electric discharge, p. 60.
- Elliott, G. A., Joshi, S. S., and Lunt, R. W.** On the velocity of chemical reaction in the silent electric discharge, pp. 57 and 74.
- Elliott, A.** See Taylor, W., and Elliott, A.
- Escolme, A. I., and Lewis, W. C. M.** Hydrolysis of the peptide ( $-CO-NH-$ ) linkage, p. 654.
- Fajans, K.** Refractometric evidence for the existence of undissociated molecules and complex ions in solutions of strong electrolytes, p. 357.
- Fells, H. A., and Firth, J. B.** Gelation of silicic acid. The formation of gas bubbles and drops in silicic acid during gelation, p. 623.

- Ferguson, A., and Vogel, I.** On the agreement with experiment of the dilution formula deduced from the Debye-Hückel theory, p. 404.
- Firth, J. B.** *See* Fells, H. A., and Firth, J. B.
- Fowler, N. R., and Mardles, E. W. J.** The decomposition of some organic substances by the electric spark, p. 301.
- Fowler, R. H.** Strong electrolytes in relation to statistical theory, in particular the phase integral of Gibbs, p. 434.
- Foxton, F., and Shutt, W. J.** The activity of zinc chloride in concentrated solution, p. 480.
- Freundlich, H.** The structure and formation of colloidal particles, p. 614.
- Garrick, F. J.** The vapour pressures of diphenyl and of aniline, p. 560.
- Glasstone, S., and Symes, T. E.** The electrodeposition of iron-nickel alloys, Part I, p. 213.
- Harned, H. S.** On the thermodynamic properties of a few concentrated salt solutions, p. 462.
- Harrison, W. R., and Perman, E. P.** Vapour pressure and heat of dilution of aqueous solutions, Parts II. and III., pp. 1, 107.
- Hartley, H., and Bell, R. P.** Notes on the Debye-Hückel theory, p. 396.
- Hartley, H., and Raikes, H. R.** The mobilities of the elementary ions in methyl alcohol, p. 393.
- Jeffery, F. H.** A method of measuring variations of electrical resistance for the determination of the thermal equilibrium diagram of the inter-metallic system, p. 563.
- Joshi, S. S.** The decomposition of nitrous oxide in the silent electric discharge, p. 227.
- *See* Elliott, G. A., Joshi, S. S., and Lunt, R. N.
- King, J. E., and Partington, J. R.** The effect of one salt on the solubility of another in ethyl alcohol solution, Part I. Part II. Quantitative discussion of the solubility of sodium iodide in the presence of sodium thiocyanate, pp. 522 and 531.
- Kraus, C. A., and Seward, R. P.** The influence of electrolytes on the solubility of other electrolytes in non-aqueous solvents, p. 488.
- Lea, F. M., and Crennell, J. T.** The action of iron as an impurity in the lead accumulator. Part I. Capacity loss due to self-discharge. Part II. Permanent capacity loss. Absorption and desorption of the iron by the positive plate, p. 269.
- Lee, W. B.** Periodic anomalies in the properties of long chain compounds, p. 634.
- Levesley, A. S.** The critical potentials of nitrogen and the nature of active nitrogen, p. 552.
- Lewis, W. C. M.** *See* Escolme, A. I., and Lewis, W. C. M.
- Lowry, T. M.** The electronic theory of valency, Part V. The molecular structure of strong and weak electrolytes: (a) Complete ionisation, p. 508.
- Lunt, R. W.** *See* Elliott, G. A., Joshi, S. S., and Lunt, R. W.
- MacInnes, D. A., and Cowperthwaite, J. A.** The ionization of some typical strong electrolytes, p. 400.
- Mardles, E. W. J.** *See* Fowler, N. R., and Mardles, E. W. J.
- Millet, H.** A note of the activity of hydrogen ion in mixed solvents, p. 515.
- Murdock, C. C., and Murdock, D. W.** The effect of series resistance on the current from a photoactive cell containing a fluorescent electrolyte, p. 593.
- Oliphant, M. L.** *See* Burdon, R. S., and Oliphant, M. L.
- Onsager, L.** Report on a revision of the conductivity theory, p. 341.
- O'Sullivan, J. B.** The behaviour of the quinhydrone electrode in solutions of neutral copper sulphate, pp. 52, 106.
- Partington, J. R.** *See* King, F. E., and Partington, J. R.
- Pedersen, K. J.** The velocity of the decomposition of nitroacetic acid in aqueous solution, p. 316.
- Perman, E. P.** *See* Harrison, W. R., and Perman, E. P. *See also* Downes, H. J., and Perman, E. P.
- Porter, A. W.** Note on the Soret effect, p. 314.
- Porter, A. W., and Rao, P. A. M.** The law of capillary flow in the case of colloids, p. 311.
- Puttick, A.** *See* Allmand, A. J., and Puttick, A.

- Raikes, H. R.** See Hartley, H., and Raikes, H. R.  
**Randall, M.** Methods of calculation of activity coefficients, p. 502  
 — The significance of the activity coefficient, p. 498.  
**Rao, P. A. M.** See Porter, A. W., and Rao, P. A. M.  
**Remy, H.** Electrolytic transference of water, true transference numbers, ionic mobilities and water sheaths of the ions, p. 381.  
**Rideal, E. K.** See Elder, L. W., and Rideal, E. K.  
**Ross-Kane, N. L.** See Wolfenden, J. H., Wright, C. P., Ross-Kane, N. L., and Buckley, P.  
**Sanderson, R. W. W.** See de Bruyne, N. A., and Sanderson, R. W. W.  
**Sato, K.** See Saunders, S. W., and Sato, K.  
**Saunders, S. W.** Investigations on gaseous explosions. Part II. Ionisation in detonating and non-detonating mixtures of hydrogen and oxygen, p. 242.  
 — Investigations on gaseous explosions. Part IV. Ionisation in methane-oxygen and acetylene-oxygen explosions, p. 256.  
**Saunders, S. W., and Sato, K.** Investigations on gaseous explosions. Part III. Ionisation in explosions of carbon monoxide and oxygen, p. 248.  
**Scatchard, G.** Mixed solutions of electrolytes and non-electrolytes, p. 454.  
**Seward, R. P.** See Kraus, C. A., and Seward, R. P.  
**Shutt, W. J.** See Foxton, F., and Shutt, W. J.  
**Symes, T. E.** See Glasstone, S., and Symes, T. E.  
**Tanner, C. C.** The Soret effect, Part 1, p. 75.  
**Taylor, W.** The actinic absorption of chlorine gas with respect to the hydrogen chlorine reaction, pp. 31, 107.  
**Taylor, W., and Elliott, A.** On the nature of the activating radiation in photochemical action, p. 583.  
 — The residual effect in the actinic absorption of chlorine, pp. 38, 107.  
**Tryhorn, F. G., and Wyatt, W. F.** A recording hydrostatic balance of simple design, p. 238.  
**Ulich, H.** Ionic mobilities in non-aqueous solvents, p. 388.  
**Vernon, W. H. J.** Second experimental report to the Atmospheric Corrosion Research Committee (British Non-ferrous Metals Research Association), p. 113.  
**Vogel, I.** See Ferguson, A., and Vogel, I.  
**Wolfenden, J. H., Wright, C. P., Ross-Kane, N. L., and Buckley, P. S.** The use of amalgam electrodes for determining activities in methyl alcohol, p. 491.  
**Wright, C. P.** See Wolfenden, J. H., Wright, C. P., Ross-Kane, N. L., and Buckley, P. S.  
**Wyatt, W. F.** See Tryhorn, F. G., and Wyatt, W. F.

# REVIEW OF BOOKS.

<b>Austin, L. S.</b> The metallurgy of the common metals . . . . .	332
<b>Baly, E. C. C.</b> Spectroscopy, Vol. II. . . . .	601
<b>Baly, E. C. C.</b> Spectroscopy, Vol. III. . . . .	680
<b>Bedford, T. G.</b> Practical physics . . . . .	108
<b>Benedicks, C.</b> Metallographic researches . . . . .	331
<b>Bone, W. A., and Townend, D. T. A.</b> Flame and combustion in gases . . . . .	977
<b>Brockman, C. J.</b> Electro-organic chemistry . . . . .	678
<b>Comber, N. M.</b> An introduction to the scientific study of the soil . . . . .	680
<b>Corson, M. G.</b> Aluminium; the metal and its alloys . . . . .	602
<b>Evans, U. R.</b> The corrosion of metals . . . . .	112
<b>Garland, H., and Bannister, C. O.</b> Ancient Egyptian metallurgy . . . . .	331
<b>Goodman, J.</b> Mechanics applied to engineering . . . . .	329
<b>Hedges, E. S., and Myers, J. E.</b> The problem of physico-chemical periodicity . . . . .	56
<b>Hinshelwood, C. N.</b> The kinetics of chemical change in gaseous systems . . . . .	329
<b>Houston, R. A.</b> A treatise on light . . . . .	329
<b>Kolthoff, I. M., and Furman, N. H.</b> Indicators; their use in quantitative analysis and in the colorimetric determination of hydrogen-ion concentration . . . . .	111
<b>Monypenny, J. H. G.</b> Stainless steel and iron . . . . .	266
<b>Painton, E. T.</b> The working of aluminium . . . . .	601
<b>Rideal, E. K., and Taylor, H. S.</b> Catalysis in theory and practice . . . . .	109
<b>Thorne Baker, T.</b> Wireless pictures and television . . . . .	268
<b>Thorpe, Sir E.</b> A dictionary of applied chemistry. . . . .	679
<b>Twyman, F.</b> The development and present position of chemical analysis by emission spectra . . . . .	268





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